

THE STABILITY OF THE ASPHALTENE AND RESIN AGGREGATES AND THEIR CHEMICAL REACTIVITY

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INTRODUCTION

The structure of the known asphaltenes can be divided into two main types: one

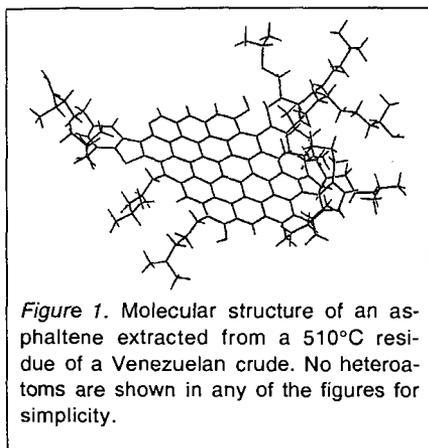


Figure 1. Molecular structure of an asphaltene extracted from a 510°C residue of a Venezuelan crude. No heteroatoms are shown in any of the figures for simplicity.

formed by molecules with a large aromatic "continent" with many rings plus alkyl branches (see Fig. 1) (1) and another composed by smaller aromatic islands connected by alkyl bridges ("archipelago" type) (2) (Fig. 2). These different 3D shapes play an important role in the reactivity of the different atoms of these molecules and in the formation and stability of the molecular aggregates or micelles that are responsible for its solubility in crude oil and residue. An analysis of the three dimensional shape of the available asphaltene molecules and of the factors involved in the stability of aggregates

formed with resins will help in the understanding of their reactivity in crude oils or residues.

THEORY

Crude oil is a complex molecular fluid that has been classified as a colloidal

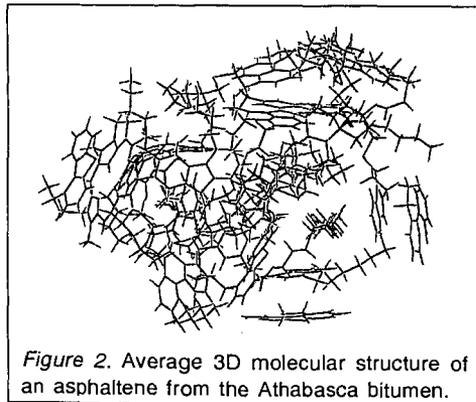


Figure 2. Average 3D molecular structure of an asphaltene from the Athabasca bitumen.

dispersion of asphaltenes in a nonaqueous solvent (3). The micelles in oil are formed by asphaltenes peptized mainly by resin molecules. Similar micelles were found in many residues of different crude oils (3b). As in all complex molecular liquids, the noncovalent interactions (van der Waals, Coulomb, and repulsive ones) (4) are responsible for the molecular recognition process that exists between the heavy

components of crude oils and residues. The resulting recognition between these molecules are very important in determining the structure and the lifetime of their aggregates (5).

MOLECULAR SHAPES AND CHEMICAL REACTIVITY

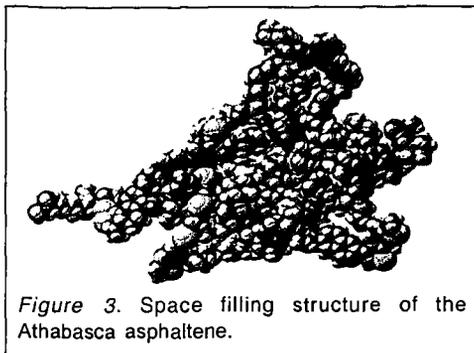


Figure 3. Space filling structure of the Athabasca asphaltene.

The acetone fraction of the asphaltenes of the Athabasca sands has been studied (6) and a 3D structure was proposed recently using molecular dynamics calculations (1) (Fig. 2). The resulting average structure showed a noticeable similarity with that proposed for an asphaltene obtained from a Boscan crude (7). On the other hand, molecules with a central

condensed aromatic core with alkyl branches were found in an asphaltene isolated from a 510 °C residue of a Venezuelan crude (Fig. 1) (1), and for several others extracted from different oils (3a).

From Figs. 2 and 3, one can see that the asphaltene from Athabasca has a very complex three dimensional form that includes cavities and tunnels of different shapes and sizes. The alkyl bridges act as elastic links between the more rigid aromatic regions that form the molecule. The final structure reflects this difference and shows a compromise between the bond and angle requirements of these two main regions. The Athabasca (also Boscan) asphaltene molecule contains a significant number of atoms that are inside these cavities or are located in places where the steric interference is high. Consequently, these sites are not always available for reactions with other molecules. This means that the number of different types of atoms obtained from elemental analysis for this kind of asphaltenes is always larger than the number that is actually available for chemical reactions. This is important in the study of the removal of atoms such as S or N because not all of them will be available for the required reactions. Clearly, not only is important to know the heteroatom content but it is also convenient to have information about its distribution for its efficient removal.

In macrocycles and other concave structures, the reactivity of atomic groups residing in the interior of molecular cavities differs from that of the same groups located on external sites (8). Significant changes were found in the acidity and other proprieties of internal and external groups in a variety of macrocycles and enzymes (8). The existence of internal cavities in asphaltenes of the archipelago type suggests that the reactivity of its atoms will depend on their relative position within these molecules and the size and shape of the internal cavities.

In the structure of lowest energy shown in Fig.2, the asphaltene molecule showed some alkyl bridges with strained bonds, C atoms with perturbed tetrahedral angles and also departures from planarity in some of its aromatic regions. The departures from the normal bond values influences the reactivity of these macromolecules. Strained bonds are weaker than normal ones and, consequently, chemically more reactive (9). Then, they are more easily broken in these asphaltenes than the unstrained ones, thus adding another factor to the complex reactivity of these molecules. In the case of asphaltenes of the continental type (Fig. 1), only the steric interference in crowded atoms will affect their reactivity as no internal cavities are present in these molecules. Consequently, the reactivity of these asphaltenes is reflected in its elemental analysis better than in the case of the archipelago type.

The formation of micelles that are peptized by resins further complicates the chemistry of the asphaltenes in residues and crude oils. Micelles are dynamic units, constantly forming and dissociating (5). For typical surfactants in water, the micelles are generated on a time-scale in the microsecond to millisecond range (5). The chemical complexity of crude oils and its residues implies the existence of many heavy molecules with different 3D shapes. These shapes influence the type, number and lifetime of the micelles of asphaltenes and resins formed in these fluids. It is expected that a polydisperse system composed by a large variety of micelles will be formed with the asphaltene and resin molecules (3b). It is difficult to estimate their lifetimes but one may reasonably assume that they are at least similar to that of the surfactants in water. The existence of these molecular aggregates adds a new dimension to the chemistry of the asphaltenes. These large molecules will not longer be available for reactions as readily as in the case of being a monomer in solution of a simple liquid. If the asphaltene solubility is low, the concentration of free molecules will be also quite small so most of them will be part of some micelle. This will have an impact in the catalytic conversion of this part of the crudes and residues because the diffusion of such micelles are much slower than for the free molecules. The resins that are located in the periphery of the micelles introduces also an additional obstacle to the direct contact of the asphaltenes with the catalysts. The strength of the asphaltene-resin interactions will determine the importance of this contribution to the availability of the asphaltenes for re-action.

The asphaltene of the continental type interacts strongly with other molecules containing planar aromatic regions (2) (Fig. 4). The large contact area produces a favorable contribution to the enthalpy of complexation of this type of asphaltenes and resins (1). The contact in the archipelago type is much smaller

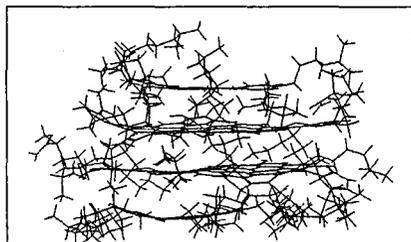


Figure 4. Lateral view of the micelle formed with two internal asphaltene molecules of Fig. 1 and two external resins molecules found in the same residue.

as seen at the bottom right of Fig. 2, where a resin is noncovalently attached to this type of asphaltene. The smaller contact area indicates the formation of weaker aggregates if all the other enthalpic and entropic factors are equal (1). This difference shows the importance of the aromatic regions in the stability of the micelles of asphaltenes and resins.

The chemical changes occurring during the cracking process modify the structure of asphaltenes and resins. As in other colloidal systems, these changes produce variations in the micelles present in the residue (5). It is important to monitor these changes and control them with conveniently design additives. They can be designed taking into account the studies of the interaction between different asphaltene and resins present in micelles of typical residues. These additives can be such that they will be able to change the properties of the resulting residue through association with the micelles and the free asphaltenes. In this way, the conversion of asphaltenes to lighter fractions can be noticeably improved.

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