



Historical perspective

Model molecules mimicking asphaltenes

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ABSTRACT

Asphaltenes are typically defined as the fraction of petroleum insoluble in n-alkanes (typically heptane, but also hexane or pentane) but soluble in toluene. This fraction causes problems of emulsion formation and deposition/precipitation during crude oil production, processing and transport. From the definition it follows that asphaltenes are not a homogeneous fraction but is composed of molecules polydisperse in molecular weight, structure and functionalities. Their complexity makes the understanding of their properties difficult. Proper model molecules with well-defined structures which can resemble the properties of real asphaltenes can help to improve this understanding. Over the last ten years different research groups have proposed different asphaltene model molecules and studied them to determine how well they can mimic the properties of asphaltenes and determine the mechanisms behind the properties of asphaltenes.

This article reviews the properties of the different classes of model compounds proposed and present their properties by comparison with fractionated asphaltenes. After presenting the interest of developing model asphaltenes, the composition and properties of asphaltenes are presented, followed by the presentation of approaches and accomplishments of different schools working on asphaltene model compounds. The presentation of bulk and interfacial properties of perylene-based model asphaltene compounds developed by Sjöblom et al. is the subject of the next part. Finally the emulsion-stabilization properties of fractionated asphaltenes and model asphaltene compounds is presented and discussed.

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Contents

1. Background	2
2. Asphaltenes	2
2.1. Structure	2
2.2. Fundamental properties	3
2.2.1. Self-association	3
2.2.2. Interfacial properties	3
3. Model compounds	4
3.1. Gray, Kilpatrick and Yarranton (2005–2008)	4
3.2. Bhattacharjee, Masliyah et al. (2008–)	5
3.3. Gray et al. (2012–)	5
3.4. Sjöblom et al. (2008–)	5
4. Perylene-based model compounds	7
4.1. Solubility	7
4.2. Interfacial properties	7
4.3. Surface forces	9
4.4. Molecular Dynamic Simulations	9
5. Emulsions	11
5.1. Dynamic surfactant concentration	11
5.2. Asphaltenes as stabilizers	11

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5.3. Model compounds as stabilizers	13
5.4. Particles as stabilizers	13
6. Concluding remarks	14
Acknowledgments	14
References	14

1. Background

Asphaltenes are typically defined as the fraction of petroleum insoluble in *n*-alkanes (typically heptane, but also hexane or pentane) but soluble in toluene [1–3]. They are typically present in concentration varying from 0 to tens of percents [4]. This fraction is responsible for different problems in oil industry that can impart the transportation (flow assurance) and the processing of crude oils. For instance:

- Asphaltenes can precipitate and give rise to organic deposition phenomena in reservoirs, wells, piping and equipment by change of pressure [5–7] or mixing with incompatible fluids [8,9]. This can lead to costly production flow restrictions and unplanned production outages.
- They are responsible for formation of stable emulsions [1] created at different stages in the oil production chain. Since these emulsions must be destabilized to get specified values of product quality (generally lower than 0.5 wt.% of water), emulsion stabilization properties of asphaltenes have been thoroughly studied [1,10–12].

From their definition it follows that asphaltenes are not a homogeneous fraction but consist of polyfunctional molecules. The complexity and unknown molecular structure of asphaltenes make the understanding of their properties difficult. Two strategies exist to overcome this problem:

- Fractionate the total asphaltene content into sub-fractions of reduced complexity. Different procedures have been used: multiple precipitation of asphaltenes with different *n*-alkane/crude oil volume ratio [13,14] or toluene/*n*-heptane volume ratio [15]; [16], ultracentrifugation [17,18], ultrafiltration [15,19]... Although this strategy is interesting, the asphaltene fractions obtained are still very complex and polydisperse.
- Develop and study model compounds, i.e. synthesized model molecules with well-defined structures similar to “average” asphaltene molecules and properties similar to real asphaltenes. This strategy represents a fundamental approach since the complexity of asphaltene composition is reduced to the study of solutions containing a single molecular species of known structure.

Over the last ten years different research groups have proposed a variety of asphaltene model molecules and studied them to determine how well they can mimic the properties of asphaltenes and the mechanisms behind the properties of asphaltenes. For instance:

- Akbarzadeh et al. [20] studied the self-association properties of derivatives of pyrene and the properties of hexabenzocoronene as a model for asphaltenes [21].
- The group of Prof. Murray Gray in Canada has studied the self-association properties of pyrene derivatives of 2,2'-bipyridine [22]. The group has also used other model compounds to study the thermal cracking and coking of asphaltenes. These model compounds were either pyrene-based molecules or derivatives of 5 α -cholestane, covalently fused to a range of differentially substituted benzoquinoline groups [23,24].
- Bhattacharjee and Masliyah in Edmonton studied different model molecules both in bulk and at interfaces by molecular modeling

(MD). The molecules studied were chosen to represent different models proposed to represent common structural and compositional aspects of petroleum asphaltenes: continental model, archipelago model and anionic continental model [25–27].

- The Ugelstad Laboratory (Prof. Sjöblom) designed first generation of asphaltene model molecules incorporating a fixed hydrophobic part with a branched alkyl chain attached to a polyaromatic core, while varying the nature of the polar group. This class of model compounds gives polyaromatic surfactants with the number of aromatic rings and molecular weights being in the range of single asphaltene molecules. Moreover a part of the structure can be modulated to determine the influence of the chemical structure. This family of molecules has been shown to account for central interfacial properties of asphaltenes [28–33].

In this review article, the different approaches and accomplishments of different schools working on asphaltene model compounds are summarized. The different experimental techniques used to study their properties will not be presented in this review, since most of them have already been presented elsewhere [34,35].

2. Asphaltenes

2.1. Structure

Crude oils are continuums of tens of thousands of different hydrocarbon molecules. Due to this complexity, characterization of a crude oil sample by determining its composition on a molecular basis is not possible even if attempts in this direction exist (domain of petroleomic [36,37]). Instead, hydrocarbon group type analysis is commonly employed [38–46]. The traditional SARA-separation is an example of such group type analysis, separating the crude oils in four main chemical classes based on differences in solubility and polarity. These groups are in terms of increasing polarity of molecules: saturates, aromatics, resins, and asphaltenes. At room temperature, saturates, aromatics and resins are liquid while asphaltenes are dark brown or black solids which do not melt.

The determination of molecular weight of asphaltenes has been the object of a long controversy [47]. Indeed the obtained results varied from few thousands to several hundreds of thousands of $\text{g}\cdot\text{mol}^{-1}$. This was a consequence of the fact that asphaltenes self-associate even in good solvents such as toluene at low concentrations ($\approx 10\text{--}100\text{ mg}\cdot\text{L}^{-1}$) [42]. Since experimental techniques used to measure the molecular weight generally required the measurements at higher concentration, the obtained results were influenced by the presence of asphaltene aggregates in the solution. For instance Small-Angle X-ray and Neutron Scattering (SAXS and SANS) experiments were generally performed at concentrations close to $10\text{ g}\cdot\text{L}^{-1}$ for asphaltenes dissolved in model solvents [17,18,48–51]. It was not until 1999, using techniques such as fluorescence depolarization technique [52–56], fluorescence correlation spectroscopy [57–59] and mass spectrometry [60, 61] that reliable results, accounting for the molecular aggregation at higher concentrations, became available. These results have shown that typical mean molecular weights of asphaltenes were $\sim 750\text{ g}\cdot\text{mol}^{-1}$ with a factor of 2 in the width of the molecular weight distribution.

Two models to describe the structure of asphaltenes have been presented in the literature: the archipelago and the continental models. In the first model asphaltenes were thought to consist of small

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