

What are asphaltenes in petroleum, oilsands, and heavy oil?

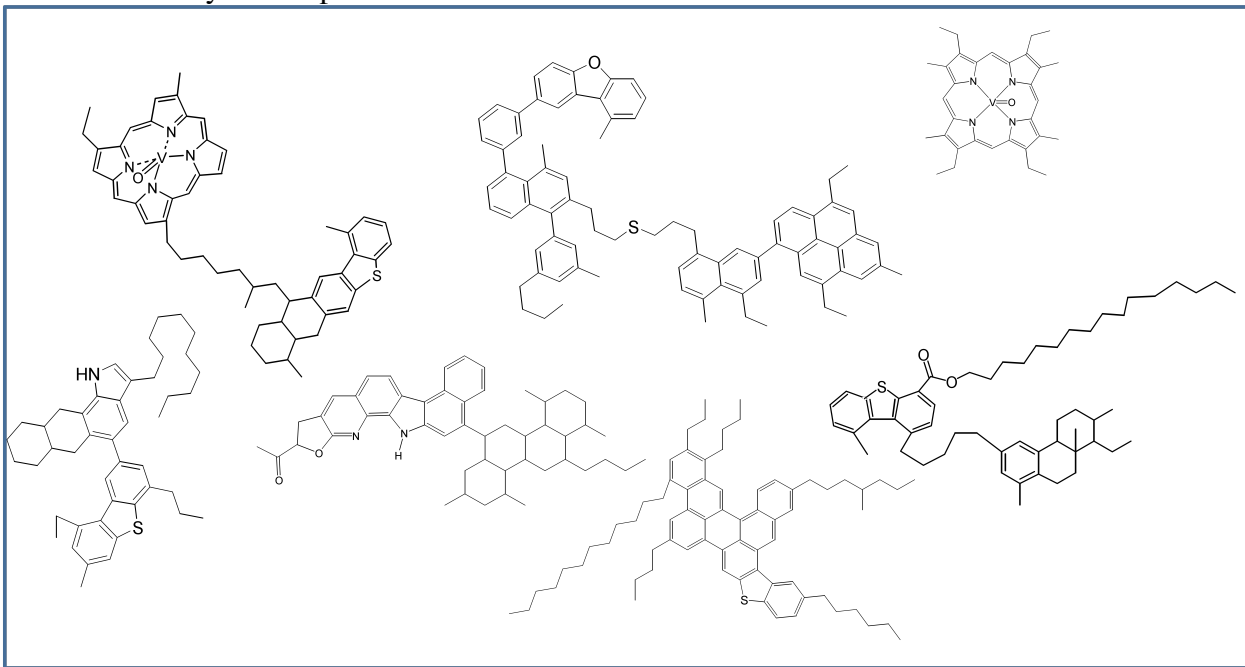
Definition

Asphaltenes are present in most petroleum materials, and in all heavy oils and bitumens from oilsands. This material is defined by solubility: the components that dissolve in toluene and precipitate in n-alkane solvents are the asphaltenes. For analytical purposes, the concentration of asphaltene in a crude oil is defined by precipitation with either n-pentane (C₅) or n-heptane (C₇).

The concentration of C₇-asphaltene in a very low density crude oil may be only a fraction of 1%, while the concentration in a dense bitumen can be over 20% of the total mass. The low solubility of the asphaltene fraction makes it very important in production and processing of petroleum. In comparison to a whole petroleum or bitumen, the asphaltenes have lower hydrogen content (4.8-8%), and a higher content of sulfur, nitrogen, nickel, vanadium, and oxygen. The low concentration of hydrogen gives a high density of 1100-1200 kg/m³, compared to circa 1000 kg/m³ for bitumen and <1000 kg/m³ for heavy oil and other petroleum.

Molecular composition

The separation of asphaltenes by precipitation gives a complex mixture of components, enriched in the least soluble components of petroleum and the components that aggregate together the most strongly. Due to the aggregation of the asphaltenes, complete molecular analysis by methods such as mass spectrometry has not yet been achieved. Pyrolysis (thermal cracking in inert gas) of asphaltenes demonstrates a complex range of attached pendant groups, including 1-3 ring aromatics and cycloalkanes¹⁻⁵. The asphaltenes are rich in ring groups, not straight chains, with a size of ring groups ranging from 1-7 rings in a single cluster. Bridges between these clusters give larger molecules and extreme diversity of composition.



Representative asphaltene molecules

How big are the asphaltene molecules?

For any complex mixture we need to consider three aspects of this question; what is the largest size, what is the smallest size, and what is the average of the population? Depending on the method that we use to determine molecular size, or molecular weight, the data may be biased toward one end or the other of the distribution. Asphaltene components tend to associate with each other; therefore, these measurements can also be systematically biased too high. The maximum and minimum sizes are both constrained by solubility. The least soluble large aromatic clusters will give the smallest asphaltenes, with molar masses in the range of 400-500 Da (i.e. molecular weight). The largest possible molar mass will depend on the geological processes that form petroleum, and on solubility in the original petroleum liquid. Direct evidence is lacking, but many researchers believe that the upper bound is in the range of 2000-3000 Da. Due to molecular aggregation, all methods of measuring the average molar mass suffer from undefined biases and errors.

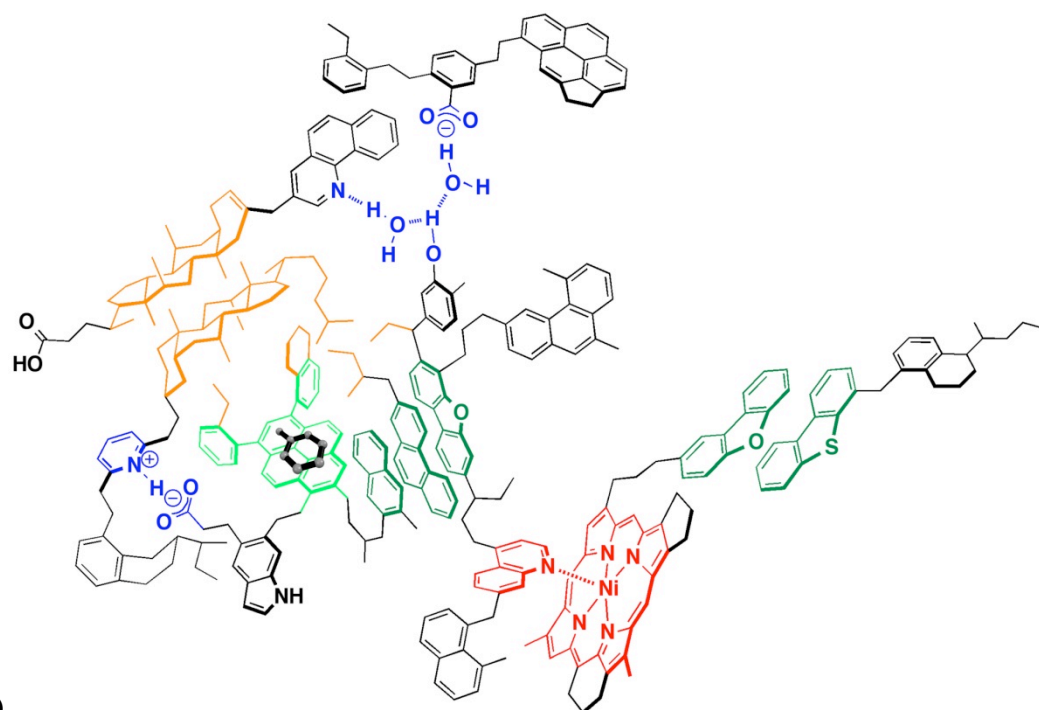
Aggregation of asphaltene components

A variety of experimental measurements show that asphaltene components aggregate to form clusters or nanoparticles over a wide range of concentration and temperature, both in petroleum and in solvents such as toluene. Many of the aggregates dissociate as the concentration is decreased⁶, or as the temperature is increased⁷, but to date the complete de-aggregation of natural asphaltene has not been verified. A range of analytical techniques put the mean aggregate size in the range of 2–20 nm^{6,8-12}.

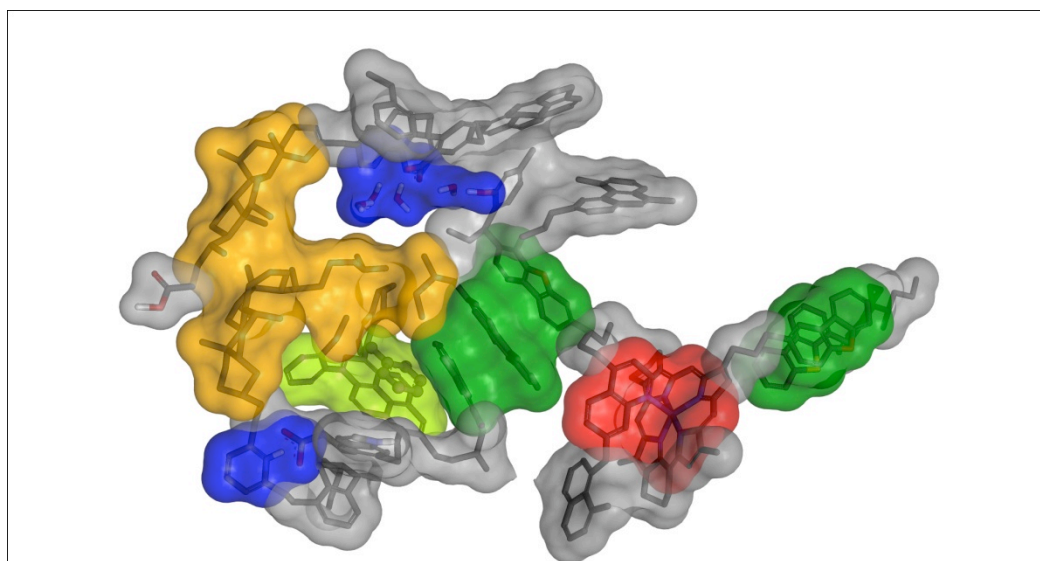
Several molecular interactions can contribute to the formation of very stable aggregates or clusters of molecules:

1. Acid-base interactions
2. Hydrogen bonding
3. Coordination complexes of metals such as vanadium
4. The association of apolar, cycloalkyl and alkyl groups in hydrophobic pockets
5. Aromatic or π - π stacking

Each of these interactions is relatively weak in isolation, but like Velcro, the combination of multiple weak links gives a strongly associated structures. A combination of acid-base interactions, hydrogen bonding, metal coordination, hydrophobic pockets, and aromatic π - π stacking can be visualized in the images below.



(A)



(B)

Associations between molecules are color coded in (A) the molecular depiction and (B) the space-filling version: acid-base interactions and hydrogen bonding (blue), metal coordination complex (red), a hydrophobic pocket (orange), π - π stacking (face-to-face dark green; within a clathrate containing toluene, light green).

These images are only representative, because the complex mixture of components in asphaltenes will give an almost limitless set of possible combinations. The size and shape of the aggregates will be highly variable, giving significant polydispersity in the population. These molecular aggregates are consistent with several important properties of petroleum asphaltenes.

- Occlusion of a range of components inside the aggregates and sufficient porosity to enable solvent access

- Strong adhesion to surfaces and interaction with smaller molecules in solution is facilitated by exposed functional groups on the exterior of the assembly. Agglomerates with multiple ring groups on the surface are consistent with irreversible binding to surfaces such as silica, while polar or charged groups on the surface would favor attachment to oil-water interfaces.
- As a network structure, the molecular assemblies can respond to external forces by compressing or undergoing elastic elongation, consistent with the mechanical properties of the asphaltene aggregates.

REFERENCES

1. Liao, Z. W.; Zhao, J.; Creux, P.; Yang, C. P., Discussion on the Structural Features of Asphaltene Molecules. *Energy & Fuels* **2009**, *23*, 6272-6274.
2. Payzant, J. D.; Lown, E. M.; Strausz, O. P., Structural units of Athabasca asphaltene: The aromatics with a linear carbon framework. *Energy Fuels* **1991**, *5*, 445-453.
3. Strausz, O. P.; Lown, E. M., *The Chemistry of Alberta Oil Sands, Bitumens, and Heavy Oils*. AERI: Calgary, AB., 2003.
4. Pelet, R.; Behar, F.; Monin, J. C., Resins and asphaltenes in the generation and migration of petroleum. *Organic Geochemistry* **1986**, *10*, (1-3), 481-498.
5. Karimi, A.; Qian, K.; Olmstead, W. N.; Freund, H.; Yung, C.; Gray, M. R., Quantitative evidence for bridged structures in asphaltenes by thin film pyrolysis. *Energy & Fuels* **2011**, submitted April 2011.
6. Mostowfi, F.; Indo, K.; Mullins, O. C.; McFarlane, R., Asphaltene Nanoaggregates Studied by Centrifugation. *Energy & Fuels* **2009**, *23*, 1194-1200.
7. Tanaka, R.; Sato, E.; Hunt, J. E.; Winans, R. E.; Sato, S.; Takanohashi, T., Characterization of asphaltene aggregates using X-ray diffraction and small-angle X-ray scattering. *Energy & Fuels* **2004**, *18*, (4), 1118-1125.
8. Dechaine, G. P.; Gray, M. R., Membrane Diffusion Measurements do not Detect Exchange Between Asphaltene Aggregates and Solution Phase. *Energy & Fuels* **2011**, *25*, 509-523.
9. Chianelli, R. R.; Siadati, M.; Mehta, A.; Pople, J.; Carbognani Ortega, L.; Chiang, L. Y., Self-Assembly of Asphaltene Aggregates: Synchrotron, Simulation and Chemical Modelling Techniques Applied to Problems in the Structure and Reactivity of Asphaltenes. In *Asphaltenes, Heavy Oils, and Petroleomics*, Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G., Eds. Springer: New York, 2007; pp 375-400.
10. Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiyagarajan, P.; Sato, S.; Takanohashi, T., Aggregates structure analysis of petroleum asphaltenes with small-angle neutron scattering. *Energy Fuels* **2003**, *17*, 127-134.
11. Overfield, R. E.; Sheu, E. Y.; Sinha, S. K.; Kiang, K. S., SANS study of asphaltene aggregation. *ACS Div. Petrol. Chem. Prepr.* **1988**, *33*, 308-313.
12. Storm, D. A.; Barresi, R. J.; Sheu, E. Y.; Bhattacharya, A. K.; DeRosa, T. F., Microphase behavior of asphaltic micelles during catalytic and thermal upgrading. *Energy & Fuels* **1998**, *12*, (1), 120-128.