

## Physical properties of asphaltenes

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Asphaltene molecules in petroleum feeds and products, which are defined by their solubility class. Their behavior can be explained in terms of chemically heterogeneous molecules in, or precipitating from, solution. In a liquid phase of unlike molecules thermodynamically near phase separation, strong concentration heterogeneities will necessarily occur due to local interactions. The dynamics of these concentration fluctuations will be controlled by the viscosity and the strength of those interactions. With the wide range of molecular types, the interactions will range from very strong to weak, and with viscosities spanning nearly 10 orders of magnitude, (dilute solutions to vacuum resid) and temperatures from sub-ambient to >400C processing conditions. Thus, there will be some situations where some associations may be relatively static, but others where they are highly dynamically dis-/re-associating.

What is important, is the instantaneous statistical average size of the clustering, regardless of whether the individual cluster is ephemeral. If molecules thermodynamically "want" to be (at any given instant) associated with a number of others, then those molecules will have a thermodynamic barrier to pass through a narrow pore. Thus, selection by size does not require permanent aggregates. Similarly we will show that the response of molecules to a gravitational field will be determined by their instantaneously averaged state of association. Thus ephemeral concentration fluctuations can indeed be concentrated by centrifugation.

Although shown to be problematic, there are those who continue to advocate a colloidal picture of asphaltene behavior, with the colloids being sometimes called nano-aggregates. Their fixed size is one of the basic assumptions in colloids, yet it is clear that the "colloid size" necessary to explain asphaltene behavior must vary with the nature of the solvent oil and the thermodynamic conditions; and as we will show, the definition of the asphaltene themselves.

Asphaltene molecules typically consist of aromatic and aliphatic functionalities. If these were severed from one another they would phase separate. Because they are connected, analogous to behavior in block co-polymers, the asphaltene molecules would be expected to exhibit local micro-phase separation, where aliphatic and aromatic regions would cluster up to a length scale allowed by their packing. One can also consider this spinodal decomposition, arrested by the connectivity of the parts of the molecule. Thus the asphaltene-rich phase would be expected and indeed does show such structure with a short-range ordered periodicity. Where concentration fluctuations occur,

this length scale would come into play especially when the correlation length is comparable. This then is the origin of the "nano-aggregate" length scale. However this would be very much affected by the details of the molecular architecture. We will show how this length scale varies as a function of the heptol fraction used to precipitate the asphaltene molecules.

The temperature dependence of viscosity of liquids is known to follow the Modified Arrhenius equation (VTF or WLF), with a divergence at low temperature being associated with a glass transition; (simple Arrhenius behavior being a poor approximation). The strong temperature dependence of the viscosity in heavy oils and other asphaltene systems also follows that behavior, with the rise at low temperatures associated with a glass transition phenomena, or Kauzmann temperature. The blending behavior as the oil is diluted can be explained as plasticization. This temperature dependent behavior cannot be explained by a colloidal treatment of viscosity (such as the Einstein relation).

Since asphaltene molecules are a solubility class from a potentially wide range of possible molecules; it is very useful to consider the molecular distribution on a 2D map of MW and solubility parameter (or any other metric incorporating aromaticity & polarity. Equivalent solvency for a species can be obtained by trading MW for s.p.; but a whole range of materials from lower-MW molecules with predominantly a PNA core, to an aromatic-aliphatic "archipelago" structure or even a polymer like polystyrene, fulfill the solubility criteria.

The community of people interested in asphaltene molecules are not limited to the study of dilute solutions of "virgin" crude oil asphaltene molecules at ambient conditions. Asphaltene molecules of interest cannot be drawn as a single type/typical/most-probable structure; and a framework to understand their behavior must include the distribution of all types of possible asphaltene molecules. Besides the wide range of geochemistries giving rise to crude oil asphaltene molecules, the processes/conditions to which these molecules are subject, and of interest to us, which result in dealkylation, aromatization, oxidation and dimerization, allow for populating all parts of the potential asphaltene compositional space. Therefore a framework for understanding asphaltene molecules cannot be limited to a single type of molecular architecture, be it "island", "archipelago" or linear chain; but must be sufficiently general.

### References

- [1] Sirota, E.B., 2005. Energy and Fuels 19, 1290-1296; Sirota, E.B. Lin, M.Y. 2007. Energy & Fuels, 2007. 25: 2809-2815