Understanding Heavy Oil Molecular Functionality and Relations to Fluid Properties

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Abstract
Often viscosity is mentioned as the single most important physic chemical fluid property of a heavy oil in terms of production. Viscosity, adherence to reservoir rock, water emulsification (amongst others) have all been known for decades to be related to the presence of N,S,O components. In the thermodynamic modeling of phase behavior and property prediction NSOs have a major impact on e.g. critical properties but the actual impact is often omitted. These constituents interact via functional groups and specific interactions with other molecules. In HO where more than 50 % of the oil cannot be distilled, the separation, identification and quantification of these compounds become difficult or impossible. Often one will observe that hydrocarbon structure is discussed in details (e.g. asphaltene structures) while NSOs are discussed in general terms. Specific chemical reactions or additives with specific interactions reveal how 3D structural networks can be broken to diminish molecular interactions and thereby e.g. viscosity. The paper will review work done using asphaltenes altered by “chemical surgery” removing specific functional interactions applying techniques such as titration calorimetry and fluorescence spectroscopy combined with data on effect of additive solvents on viscosity, and place this in the context of understanding heavy oils and fractions of petroleum. This will show how determination of specific interactions (functional groups) may be very useful indeed and even more important than understanding hydrocarbon structures in heavy fractions.

Introduction
The majority of works related to heavy oil properties needed for the optimization of both recovery, transport and refinery of heavy oils are concerned with the hydrocarbon structure as well as the overall NSO content of the material. Heavy oils contain large amounts of asphaltenes and properties are to some extent dominated by this fraction. Much of the focus the last century or so has been concerned with the impact of hydrocarbon skeleton structure of this material on these properties (viscosity, density, tendency to form solid phases etc.). However, it has for the same period of time been well recognized that the content of N, S, O containing species is also abundant in heavy oils and residues. They tend to concentrate in high boiling fractions as well as in solvent separation fractions (resins and asphaltenes). From chemistry of natural products and pure compounds it is well known that these heteroatoms (different from H and C) may engage in specific interactions with a significant impact on physical properties. See below. Only variations in solid phase crystallinity amongst pure hydrocarbon isomers may have such an impact. Hence heavy oil properties needed to improve production, transportation and refining is determined to be linked to a better understanding of the impact of specific interactions and how to control these. This paper reviews work seeking to understand this in connection with heavy oil, asphaltenes and resins.

Discussion
In petroleum science and especially heavy oil and residue chemistry asphaltene content and chemistry is abundantly discussed. The chemistry of asphaltenes is mainly described as aromatic, and aromaticity is in most works proposed as the
driving property leading to amongst other asphaltene flocculation and precipitation. While we may indeed class asphaltenes as belonging to aromatic substances (with about 50% Carbon in aromatic structures) we must also acknowledge that asphaltenes contain a larger fraction functional groups rendering these types more insoluble than pure hydrocarbons, providing them with the ability to cross link (gel) the fluid as well as surface active. The latter leading to both wettability issues as well as emulsion stabilizing ability. Something that pure hydrocarbon structures do not possess.

The present work seeks to show the role of functionality of asphaltenes and other molecules such a resins on fluid properties. These are properties and molecular behavior that hardly can be linked to the aromatic nature of these materials. Over the years we have made experimental studies in which property-structure-chemistry relations were investigate by removing fractions by extraction or by what we may call chemical surgery specific functional groups are removed or blocked before property estimation. Most of the work has been performed on separated asphaltenes but the results can be extrapolated to the role of any petroleum molecule carrying a specific functionality such as resins. In Figure 1 two molecules which could be resins or asphaltenes are shown. These molecules have been synthesized and the solubility determined. As indicated the less complex molecule but with the ability to cross link is the one insoluble in pentane, hence as per definition this would be an asphaltene.

**Molecular properties of model molecules.**

To set the stage further we look at the impact of functionality on different properties of molecules with similar hydrocarbon structure, Table 1. As observed hydrocarbon structures may affect especially melting points (and therefore also solubility) but boiling points are in general similar for HC isomers. The anthracene and phenanthrene isomers are classical examples where phenanthrene has a high degree of crystalinity in solid state. It also has about 22 times less solubility in common solvents compared to its isomer. On the other hand if functional groups are introduced in a structure a large impact is observed. Introduction of a hydroxyl group may result in significant melting and boiling point increases and hence results from i.e. gas chromatographic analysis may be altered substantially leading to wrong determination of molecular distributions, property estimation and thereby poor thermodynamic modeling for production planning and process design. Introduction of the carboxylic acid functionality further increase boiling and melting points.

**Specific Chemical Conversion**

In the work by Juyal, Merino-Garcia, and Andersen (4,5,7) asphaltenes were subject to specific chemical alteration. Asphaltenes were separated from oils using heptanes according to a modified IP143 procedure. All separations were performed at room temperature, followed by vac. Filtration and extensive washing/extraction assisted by ultrasonication. 5 Types of chemical alterations were performed as illustrated in Table 2: 1. Methylation which blocks all hydrogen bonding sites of the primary type mentioned above; 2. Silylation which blocks COOH and OH; 3. Reductive alkylation which breaks heterogeneous bridges (S and N while inserting in this case butyl chain; 4. Reductive hydrogenation which breaks similar heterobonds but introduces hydrogen attached to the hetero bonds theoretically leading to smaller size but increase hydrogen bonding sites. 5. Finally a Friedel-Craft octylation was done where octyl groups are substituted into aromatic structures at the position of aromatic hydrogen. The latter results in a “hairy molecule”. By performing these types of conversions chemistry 1 and 2 give rise to lowering of H-bonding capability while maintaining the “central” hydrocarbon structure. If the functional groups played a minor role in interactions on should expect a likewise minor change. Reductive chemistry leads in general to breaking of molecules. If central single island type of asphaltene were present we would not observe large changes if any. This is also known from hydrotreating of residues where smaller aromatic structures are released from asphaltenic material (6). Chemistry 4 gave rise to H2S evolution indicating that sulfur bridges could be present, unfortunately the amount could not be quantified.

One feature to show the impact of functionality is emulsion stability. The impact on emulsion stability is indicated in Figure 2 for a series of differently converted asphaltenes. Asphaltenes of different origin showed similar results regarding the role of functionality at the interface. As can be seen total removal of H-bonding capacity to a large extend removes the capability of asphaltene to stabilize emulsions. This should not come as a surprise but the fact that blocking only OH/COOH has minor effects was not expected. What was more surprising in this work was that the removal of OH/COOH led to an increased instability of the asphaltene in terms of precipitation (4). The analogy of this test with any surface interaction is obvious; be it reservoir rock, well and surface facility surfaces.

Titratation calorimetry (ITC) can be used to monitor heat of interaction between molecules and has been mainly used in biochemical research. It has however, successfully been applied to petroleum as well. The above chemically changed molecules were subject to ITC (Andersen and coworkers 4,5,7). This showed as indicated in Figure 3 that in agreement with the emulsion studies heat of interaction between individual molecules were changed significantly and to different degrees both related to the origin and the molecular alteration.

Further fluorescence spectroscopy showed a decrease in the molecular interactions upon methylation. This was seen as an increase in emission at lower wavelength after the reaction. Strong molecular interaction normally leads to quenching of low wavelength emissions.

The above work indicates that functionality indeed plays a role not only in the stability of asphaltenes but also in the way these molecules interact (asphaltene-with-asphaltene and/or resin-with-asphaltene) or with other polar compounds in the maltene fraction. It follows from this that asphaltene should not solely be described by the aromaticity which is the primary descriptor used in the current scientific literature. Hence, oils the functional groups need to be taken into account, in order to understand how these molecules relates leading to interaction affecting the transport properties of.

**Viscosity relations**

Gould et al. (2) made silylation of coal liquefaction bottoms and found a significant drop in the viscosity similar to our findings above on the interaction amongst molecules. As this is
not affecting asphaltene size or hydrocarbon structure it points at specific interactions as an important contribution to viscosity of HO.

Zeng et al. (3) recently performed a study into the viscosity of heavy oils when mixed with compounds that can interact with “acidic and basic sites”. We observe in this interesting study that viscosity is strongly related to acidic sites which may also be described as hydrogen bonding sites. The relative decrease in viscosity for two heavy oils compared to addition of 1 wt % toluene was 15 % more reduction upon adding an amine. This means that H-bonding and acid base interaction are very important in structuring and increasing viscosity relative to a hydrocarbon-only mixture. Toluene only has a diluting effect while additives molecules investigated can block sites and breaks the structure. Again this supports the notion that a better characterization of functional group content and interaction could be valuable not only in fundamental understanding of heavy oil structuring but also in prediction of properties needed to design production and processes. We also know from a large data base of HO properties that asphaltene content alone is not the single most important parameter in determining viscosity. Recent studies from Wang et al. (1) have indicated that asphaltene play a minor role compared to acidic molecule which are more important on accord with our findings above.

Conclusions

The purpose of this paper has been to emphasize the role of functional groups in the determination of heavy oil properties. This is as indicated from analogy with pure components not new insight, but often the search goes for simple correlation with parameters such as SARA content or similar. In reality the above only points in the direction of acidity leaving out the other functional groups. The work by Zeng et al. (3) provided evidence of acid-base relations. We therefore still need to understand fully the role of sulfur and nitrogen species, and their involvement in structuring of heavy oils. As indicated above they seem to be more important for the emulsion stability while the results were inconclusive using ITC.

Acknowledgement

The contributions from Drs. Daniel Merino Garcia (Repsol) and Priyanka Juyal (Nalco) as well as former colleagues at Dept.Chem.Eng, Technical University of Denmark are highly appreciated. Likewise the author is grateful for the insight into the work of colleagues Drs. Huang Zeng and Geza Horvarts Szabo both Schlumberger DBR Technology center.

References

3. ZENG, H., ZABEL, F., SZABO, G.H., BULAVA, M., ( to be published)

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Table 1. Molecular structures and impact of substitution on melting and boiling points.
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<td>5. Alkylation Octylation</td>
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Table 2. Schematic reactions performed on heptanes asphaltenes.

A: pentane insoluble  
B: pentane soluble

Figure 1. Relations between structure and solubility. The presence of oxygen on A makes it insoluble in pentane. Data provided by Dr. Frederic Tort, Total Solaize, personal communications.

Figure 2. Model emulsion stability. Asphaltene stabilized emulsions of 50% water and 50% toluene with 1% asphaltene added. Stability after 10 hrs. Abbreviation indicates neat asphaltenes, methylated, silylated, butylated, reduction, and octylation.