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Small angle scattering and asphaltenes

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Abstract

Petroleum is a mixture of organic material consisting of a series of molecules with increasing molecular weight but with decreasing carbon to hydrogen ratios. This monotonic trend leads to distinctive properties of each class, cut by solvents. Asphaltenes are a class soluble in toluene but not in heptane. The importance of asphaltenes lies in their relevance to petroleum operations. Many properties of petroleum liquids are due to the interplay between asphaltenes and other co-existing components. These complex interactions impact on petroleum phases, and thus the operations. So-called petroleomics is a scheme to link the molecular structures of the most relevant components in the petroleum liquid to its overall properties, similar to the proteomics widely accepted in biological sciences. However, though the asphaltene molecular structure and compositions are relevant to the macroscopic properties of petroleum liquids, their aggregates on the colloidal length scale could be the most relevant elementary unit that dictates the properties of the petroleum mixtures. In this regard, it is legitimate to use small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) techniques to bridge the molecular structures of asphaltenes and the operational parameters that are commonly applied in the field. In this review, the linkages between asphaltene molecules and their aggregates and the asphaltene aggregates and the macroscopic properties are described. Applications of small angle x-ray and neutron scattering for characterizing asphaltene aggregates and asphaltene emulsions are also discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The intent of petroleomics is to address large length scale physical and chemical properties of petroleum liquids and solids using the molecular structure of the components comprising them. This approach is similar to using statistical mechanical theory for describing the macroscopic properties of a system, for example, using the inter-particle potential and structure factor to characterize viscosity [1–3]. This is generally applicable when adequate molecular information is available and proper linkage between the structures and the properties established. For

surfactant systems, it is much more feasible because the molecular structures are well defined. Modelling of their aggregate structures and properties at various thermodynamic conditions is much easier. To adopt this philosophy and technology for complex systems like asphaltene and petroleum liquids is a challenge. First, detailed molecular information should be available as the starting point. For the most refractory and complex components of petroleum material like asphaltene, it has been difficult to unambiguously identify their molecular structures until recently [4, 5].

Since the molecular information is available, the time is right for looking into the possibility of building petroleomics, in spite of many stumbling blocks ahead. This development is in many ways similar to the Human Genome Project where genes were identified and characterized. In order to apply knowledge about genes for developing drugs, there is still a need to map out the correlation between genes and diseases. The apparent symptoms of a disease, though it has a quantitative link to each involved gene, only exhibit their integration effect. Limited known cases to date suggest that the attributes of each relevant gene are distinctive and its 'contribution' to the disease is almost unmeasurable. This expected yet unexpected outcome had slowed down the gene treatment and drug development pace. Since each disease only shows the symptoms as the integrated properties, these properties have to be de-convoluted, in order to identify how the relevant genes are involved. Mathematically, this is equivalent to extracting a set of parameters from their integrated value. It is theoretically not possible to find a single set of parameters, as we know that the number of eigenfunctions is often infinite. The specific one-to-one key-and-lock relations in bioprocesses significantly reduce the number of parameters, making the de-convolution much more feasible. Thus, using genes to link to integrated effects, such as disease symptoms, is in principle possible though it still poses a great challenge.

Knowing this fact in the Human Genome Project and proteomics, it becomes obvious that if petroleomics is to be practical one day there is a need to develop linkages between the smallest length scales, i.e. the molecular length scale, and the macroscopic scale parameters, such as viscosity, which engineers deal with in the oil field.

If the linkages exist it is possible to completely describe the properties of petroleum liquids using molecular structures. However, this is not the case. Unlike proteomics, where reactions are specific and structurally controlled, the integration of petroleum components into the crude oil forms, including asphaltenes, is essentially not possible to define. Under this circumstance, using a set of integrated parameters with known linkages to the molecular structures as the fundamental parameters is much more practical. One such set of parameters is the colloidal structures formed by natural aggregation of the more refractory component, the asphaltene.

Asphaltene is an essential component during oil production because its solubility in the crude oil directly impacts petroleum operations. Asphaltene tends to self-assemble into nano-scale aggregates. These aggregates do not grow upon increasing concentration. They flocculate when concentration is substantially high (~ 8 wt%). However, asphaltene only forms a portion of petroleum liquids. It may not represent the overall characteristics of petroleum liquids. In this regard, using integrated parameters, such as the colloidal structures and characteristics of the asphaltene aggregates, can be more representative than asphaltene molecular structures even though they are not the primary parameters. There are a number of such non-primary parameters, including size, shape, structural factors, and polydispersity of asphaltene aggregates. They can serve as functional parameters to derive the rest of the field and operational parameters. To do so, three conditions should be met. Firstly, these parameters should be well characterized for asphaltene aggregates. Secondly, they should be fully describable by asphaltene molecular structures. Finally, these parameters should be relevant to the overall properties of the petroleum liquids in the field.

To identify and characterize these parameters, techniques that measure the right length scale are needed. Asphaltene aggregates are in the colloidal length scale between 5 and 1000 Å. Thus, small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) are credible techniques. Both techniques have been applied to a number of colloidal systems with good success [6–11]. In this review, small angle scattering work on asphaltene systems will be discussed. The limits, spectroscopic configurations, and data analysis schemes will be described.

2. Asphaltene aggregation

Asphaltene aggregation has been a subject of interest for many decades since it was identified in the early 20th century, partly because of its significance in petroleum processing and partly because of the parallel development in colloidal science. To date, the energies that drive asphaltene aggregation are still a research topic.

The techniques used for detecting asphaltene aggregation can be categorized into surface techniques and the bulk techniques [12]. The bulk techniques are more convenient if the intent is to identify the aggregation phenomena and characterize the aggregates [13] in terms of their sizes and polydispersity. There are no known techniques that can simultaneously detect asphaltene aggregation onset and in the mean time characterize the properties of the aggregates. It requires more than one technique. It also needs multiple theories to construct the relationship between the measurable data and the state of the system. As a result, a set of theories may be used to extract information regarding aggregation onset, while other sets of theories are needed for characterizing the aggregates. Small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) certainly meet the requirement for characterizing the aggregates and to provide information for further thermodynamic analyses. Since the focus of this review is on structural characterization of the asphaltene aggregates, the aggregation phenomenon will not be discussed. Details of asphaltene aggregation are well documented [11].

3. SAXS and SANS

SAXS makes use of the electron density difference to identify and measure the particle size, shape and polydispersity on the colloidal scale. Asphaltene aggregates and their surroundings, either solvents or petroleum liquids, may differ in their electron density. If the electron density contrast is high enough, it is possible to detect the asphaltene aggregates in crude oils. In 1940, Pfeiffer and Saal proposed the resin-peptized model to explain suspension of asphaltene in petroleum liquids [14]. If this argument is correct, one should be able to ‘see’ the suspended asphaltene aggregates using SAXS. It turns out that most asphaltenes contain heteroatoms, making the electron density contrast just high enough to detect. However, long data acquisition time is often needed to collect statistically significant data. This requires the instrument to be stable and the configuration well selected.

SANS applies a similar principle to SAXS except the contrast for SANS to detect an object from its surroundings is the scattering length densities, which depends on the difference of the nuclei that comprise the molecules. In asphaltene systems, it is the difference of the neutron scattering cross section between the asphaltene molecules and the surrounding molecules. Asphaltenes generally do not have enough contrast for neutrons to distinguish them from their surrounding molecules. One thus needs to dissolve the asphaltene in deuterated solvents to enhance contrast for SANS measurements. Other than the contrast difference SAXS and SANS apply essentially the same scattering theory and share many data analyses schemes.

As the wave passes through the system they are scattered by the suspended asphaltene particles and the solvent molecules in different manners such that the scattered spherical waves will leave the system at different angles. Mathematically, this scattering distribution function can be expressed as

$$f_m(\vec{Q}) = \rho_m(\vec{r}_m) e^{i\vec{Q}\cdot\vec{r}_m} \quad (1)$$

where \vec{Q} is the scattering vector (or momentum transfer from the initial state to the final state) with a value of

$$|\vec{Q}| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (2)$$

for an incident wave of wavelength λ , and \vec{r}_m is the position vector where the scatter resides at the time when it interacts with the incident wave. Equation (1) is for a particle of no size only. For finite size particles, equation (1) can be extended to

$$f_M(\vec{Q}) = \int_M [\rho_j(\vec{r}_j) - \rho_{\text{solvent}}] e^{i\vec{Q}\cdot\vec{r}_j} d\vec{r}_j \quad (3)$$

Essentially, equation (3) is an integration of equation (1) over the particle M that has a size effect on scattering. Once the scattering function is known, the expected value of the scattering function can be obtained.

$$P(|\vec{Q}|) = \langle |f_M(\vec{Q})|^2 \rangle. \quad (4)$$

Equation (4) is the scattering intensity distribution function from one non-zero size particle. This is known as the form factor. It carries the size, shape and polydispersity information of the particles in the system but in a coupled form. In order to extract information about the size, shape and polydispersity individually, proper decoupling schemes are needed.

In addition to the size effect, the form factor, the scattering intensity distribution function is also affected by the interactions among particles. The factor governing these interactions is called the structure factor, $S(Q)$. The overall scattering function taking into account both interactions can be expressed as

$$I(\vec{Q}) = \frac{1}{V} \sum_{k=1}^{N_p} \langle |f_k(\vec{Q})|^2 \rangle + \frac{1}{V} \left\langle \sum_{k=1}^{N_p} \sum_{\substack{k=1 \\ j \neq k}}^{N_p} f_k(\vec{Q}) f_k^*(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_k - \vec{R}_j)} \right\rangle \quad (5)$$

where N_p is the number of particles and V is the total volume of the system. The first term of equation (5) is the contribution from the form factor as given in equation (4) and the second term is from the structure factor.

If the particles are monodisperse in size, equation (5) can be simplified to

$$\begin{aligned} I(\vec{Q}) &= n_p \left\langle |f_k(\vec{Q})|^2 \right\rangle \left\{ 1 + \left\langle \sum_{k=1}^{N_p} \sum_{\substack{k=1 \\ j \neq k}}^{N_p} f_k(\vec{Q}) f_k^*(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_k - \vec{R}_j)} \right\rangle \right\} \\ &= n_p P(\vec{Q}) S(\vec{Q}). \end{aligned} \quad (6)$$

For an isotropic system, $S(\vec{Q})$ can be expressed by averaging over the angle,

$$\langle S(\vec{Q}) \rangle = S(Q) = 1 + 4\pi n_p \int_0^\infty [g(r) - 1] \frac{\sin Qr}{Qr} r^2 dr \quad (7)$$

where $g(r)$ is the so called pair distribution function representing the probability of finding a particle at distance r when there is a particle at the origin. It is essentially the local number

density of the particles. $g(r)$ is the most essential function that links the thermodynamics of the system to the structure factor which can be determined from a scattering measurement.

The above description clearly indicates that there are two major factors to be determined in any scattering experiment. They are the form factor $P(Q)$ and the structure factor $S(Q)$. $S(Q)$ is equal to unity if the system is very dilute [15] or the particle–particle interactions are substantially short range. For asphaltene solutions, the media are organic solvents with very low dielectric constants. The inter-particle interactions are very short range. In the cases discussed here the asphaltene concentrations are low (<5%); $S(Q)$ can thus be taken as unity and only $P(Q)$ needs to be dealt with.

A further simplification of the scattering intensity distribution function is to apply an approximation for particle size and shape characterization. For example, the $P(Q)$ can be approximated by the radius of gyration using the Guinier plot,

$$I(Q) = I_0 e^{-Q^2 \frac{R_g^2}{3}}. \quad (8)$$

Using equation (8) one can plot the logarithm of $I(Q)$ versus Q^2 to evaluate the radius of gyration R_g . Once the radius of gyration is determined, the dimension of the particle can be calculated if the shape of the particle is known. However, the Guinier plot only provides the radius of gyration, not the shape of the particles. To determine the shape of the particle, other analyses are needed. There are several approaches to determine particle shape. One is to use the Porod plots [9] to look for the linear regions using a cylindrical system or a system with flat particles. These analyses, however, are rather limited.

Another approach to determine the particle shape is to presume the shape of the particles. Using the presumed shape, the corresponding $P(Q)$ can be rigorously calculated with the dimensional parameters built in. The calculated $P(Q)$ can then be used to fit the scattering data, from which the structural parameters can be extracted. Using this approach often requires justification of the presumed particle shape. Mathematically, it requires another axis along which the functional form is well defined. In this way, one can use the extracted particle dimension and the presumed shape to evaluate this parameter along that particular axis to see if the parameter indeed shows the functional behaviour it is supposed to. In a previous report [17] we show this method using concentration as the axis and the contrast as the parameter.

Finally, one can also determine the shape by presuming the particle shape for data fitting and then calculate the invariants to see if the presumed shape is correct. This method was discussed in detail in a previous report [16]. Finally, one can directly invert the scattering function to obtain the distance distribution function, $p(r)$, which represents the distribution of the scattering density. It provides direct information about the scattering object and shape can be mapped out this way. Brunner-Popela *et al* gave a comprehensive review of this approach [18].

4. SAXS and SANS instruments

The SAXS work presented here was performed using the 10 m small angle x-ray facility at the Oak Ridge National Laboratory. The x-ray source is a rotating anode at 4 kV and 100 mA with a copper target. The take-off angle was 6° . The monochromator for wavelength selection was a flat graphite one adjusted to select the $\lambda = 1.54 \text{ \AA}$ photons. The sample holder is a liquid cell with a double Kapton window. A 2D detector was used with a continuous wire divided into 64×64 pixels. A mechanical pump was used to maintain 10^{-4} Torr of vacuum in the spectrometer during measurements. Fe-55 (24.4% 5.9 keV and 2.9% 6.5 keV) was the standard used to calibrate the pixel-to-pixel sensitivity. Sample transmission was determined using a with-carbon and without-carbon process. The scattering spectrum obtained was in an

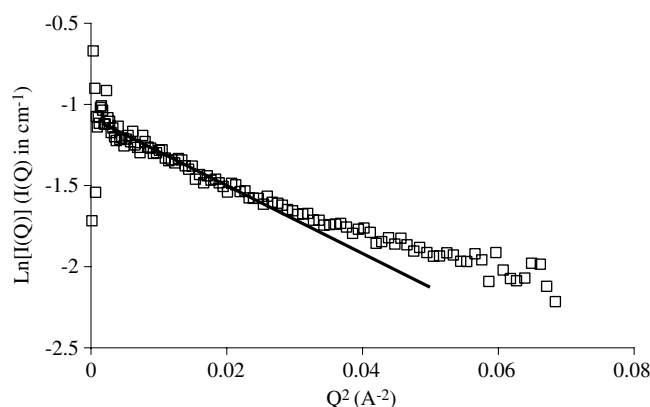


Figure 1. Guinier plot of the SAXS intensity distribution function of Ratawi resin (heptane soluble and pentane insoluble fraction) in de-asphalted oil (C5S). The radius of gyration calculated is 7.8 Å.

absolute scale of cm^{-1} representing the differential scattering cross section of the sample. It is important to obtain the absolute intensity because it helps determine the particle shape. Fitting an intensity distribution in absolute intensity is usually not possible if the model is incorrect and the number of adjustable parameters is reasonably low. This further assures the unambiguity of the data analysis.

Two SANS spectrometers were used to generate the data reported here. One was the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL). It has a Q range from 0.008 to about 0.3 \AA^{-1} , equivalent to a spatial resolution of a few ångströms to several thousand ångström particle sizes. The other spectrometer used was the 30 m NG7 spectrometer at the National Institute of Standards and Technology (NIST). It is a reactor source SANS spectrometer. The wavelength of the cold neutrons is from 5 to $\sim 30 \text{ \AA}$. Because it is a 30 m long spectrometer, the sample-to-detector distance can be adjusted from 1 m to nearly 20 m, which makes the Q range much wider (from 0.002 to 0.7 \AA^{-1}). Quartz cells were used to hold samples since the neutron has a high transmission in quartz.

5. SAXS and SANS experiments and results

There are several sets of measurements reported here; some use SAXS and others use SANS. Asphaltenes used for measurements were from Ratawi vacuum residue or Arabian medium heavy vacuum residue using the standard heptane extraction process. Briefly, one gram of vacuum residue asphaltene is mixed with 40 ml of heptane and mixed for 24 h before being filtered by Whatman No. 5 paper to separate the insoluble fraction (asphaltene) from the rest. The insoluble fraction was then dried under nitrogen until constant weight was obtained. The heptane soluble fraction was further cut by the same procedure but using pentane as the solvent. After this process, three fractions were obtained—*asphaltene (C7I)*, *resin (heptane soluble but pentane insoluble)* and *pentane soluble (C5S)*.

6. V-A SAXS measurement on Ratawi resin and asphaltene

Figure 1 shows the scattering intensity distribution function. A simple Guinier plot yields a radius of gyration of 7.8 Å. Assuming it is a spherical object [16], then the radius R

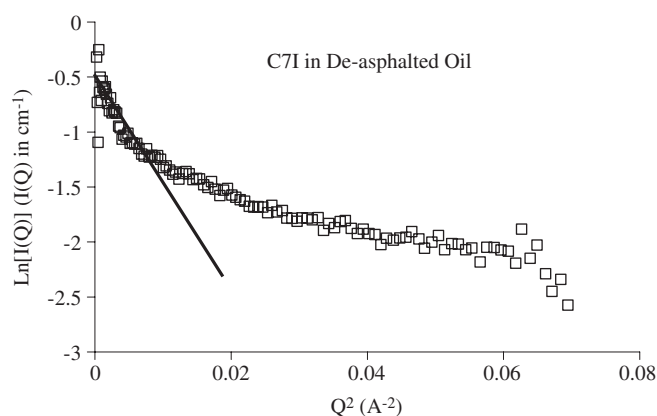


Figure 2. Guinier plot of the SAXS intensity distribution function of Ratawi asphaltene (the heptane insoluble fraction) The radius of gyration calculated is 20.7 Å.

is about 10 Å. Taking 1.25 Å as the carbon–carbon bond length, this is equivalent to less than seven carbon bond lengths. Compared with the recent asphaltene molecular structure proposed [4, 5], it is reasonable to argue that this is not an aggregate. It is more of the average size of a resin molecule (the heptane soluble but pentane soluble fraction). QR_g is less than unity for the range we used to derive the R_g , ensuring the legitimacy of Guinier analysis. We do not emphasize that the molecules are spherical but do believe that an exercise using a spherical object to get R is acceptable. Fluorescence emission [4] showed a similar dimension for a resin called UG8. This agreement cannot be accidental when the two mechanisms are vastly different, one by scattering pattern analysis resulting from photon–electron interaction while the other by a relaxation mechanism. The agreement must be a reflection of the true dimension of this class of material.

Figure 2 shows a 20.7 Å radius of gyration. Again, one assumes a spherical model to get 26.7 Å. This radius is considerably larger than an asphaltene molecular model and should be considered an aggregate. Fluorescence emission shows a diameter of 19.7 Å [4]. If we take this number as the asphaltene diameter, the asphaltene molecule radius can be in the range of 10–12 Å if the blue wing of the fluorescence wavelength is taken into account. Using these numbers, the volume ratio between an aggregate and a molecule is about 11–19. This is a rough estimate of the aggregation number assuming compact packing, which should not be the case as discussed below. If we take the void of the packing into account, the aggregation number can be up to 30% lower [16]. Other reports showed a range of ~25–45 Å size asphaltene particles [11]. While the individual asphaltene molecule may not vary as much, the aggregate size can vary even more due to the different compositions. Therefore, the 26.7 Å radius obtained here is well within the range.

Instead of using the Guinier plot, one can establish a form factor with structural parameters built in. Details about the form factor with polydispersity had been discussed in a previous report [16]. Using the form factor and an appropriate polydispersity model one can fit the scattering intensity distribution function and extract the radius and the degree of polydispersity. Figure 3 shows the radii extracted from such a fitting scheme using the Schultz distribution function as the polydispersity function [17]. As one can see, the asphaltene aggregates from different sources all show radii between 25 and 45 Å. The 100 wt% concentration shown here is defined as the asphaltene concentration in the vacuum residue. The actual asphaltene concentration is about 20% in the vacuum residue and the lower concentrations were made

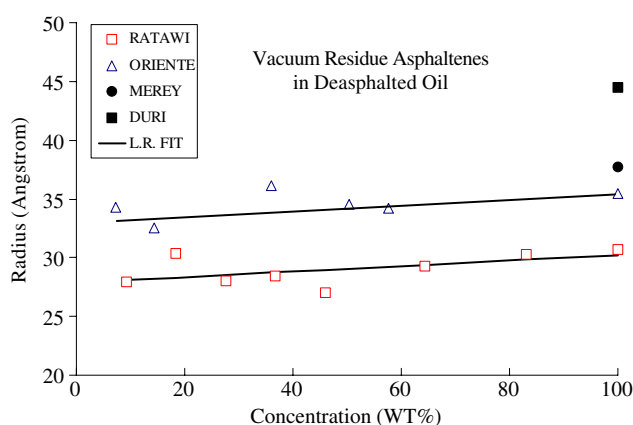


Figure 3. SAXS derived radii of Ratawi asphaltene aggregates in vacuum residue (100 wt%) and in de-asphalted oil (diluted from vacuum residue) and the radii of aggregates of various asphaltenes in their vacuum residue state.

by diluting the 100 wt% system by de-asphalted oil. Note from this plot that the aggregate size does not increase upon increasing concentration like a micellar system. It is statistically unchanged if the polydispersity is taken into account.

The relative independence of aggregate size as a function of the concentration leads to the structural evolution that Yen [19, 20] proposed many years ago. Yen proposed formation of elementary particles upon aggregation as the first step. These elementary particles do not heavily depend on asphaltene concentration. However, these particles may further aggregate to form much bigger particles in which an elemental particle maintains its own integrity and intra-particle structures. This second step of aggregation is more of flocculation than aggregation. If these secondary aggregates are much bigger than the elementary aggregates, they may not be detected by the SAXS due to the limited Q range. A much smaller Q is needed to detect these particles if they exist. Some SANS facilities can reach lower Q than the SAXS spectrometer used. In the following two SANS experiments there is some indication of the existence of large particles.

7. V-B SANS measurement on asphaltene aggregation, emulsion and dispersant effect

Figure 4 shows 1% (wt) Ratawi asphaltene solution in deuterated toluene/pyridine mixtures. The curves were vertically shifted for clarity. The extracted particle sizes are similar in all mixtures and are in the nano-range. Since both toluene and pyridine are good solvents for asphaltenes, the extracted particles sizes likely represent the elementary particles described in Yen's model, or the smallest aggregates.

It should be noted that the radii of gyration obtained from figure 4 are from $Q = 0.015$ to 0.023 \AA^{-1} . With 30 \AA as the radius of gyration the $R_g Q$ is equal to $0.45\text{--}0.69$, much smaller than unity, justifying the applicability of the Guinier approximation. Although the range used is not the lowest range, there is no lowest range. It is defined by the experimental set-up, thus, the $R_g Q$ value should be the value used to justify the result. For lower Q (i.e. less than 0.015 \AA^{-1}) the intensity increases rapidly, indicative of much larger objects. Guinier analysis shows they are about 120 \AA . This is likely the further agglomeration of the elemental particle of 30 \AA . The main message from these curves and Guinier analysis is that the elementary particles are

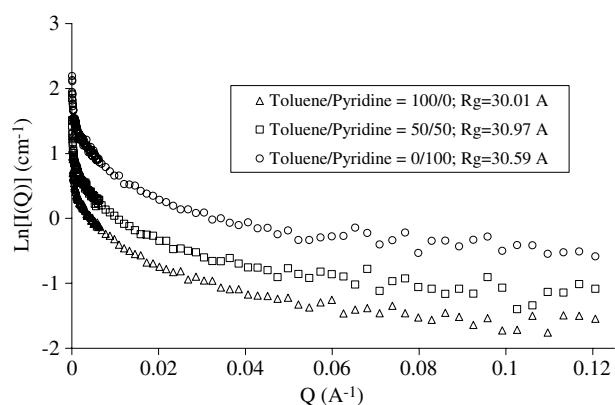


Figure 4. 1% Ratawi asphaltene in toluene/pyridine mixtures.

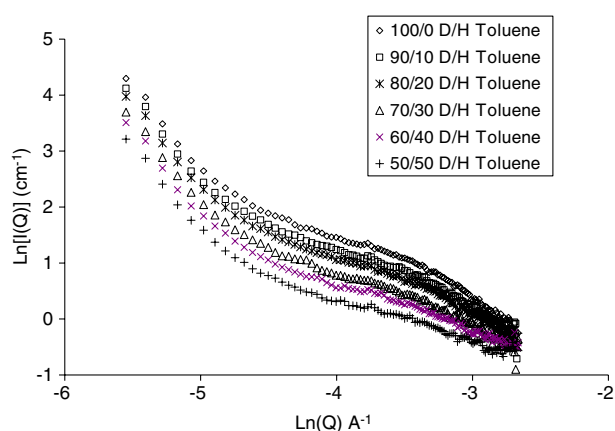


Figure 5. Contrast variation measurements for series of D-toluene/H-toluene mixtures. The asphaltene concentration is 1%.

about 30 Å and do not increase upon increasing asphaltene concentration. A similar conclusion was drawn in a previous report [11].

Because SANS uses deuterated solvents (D-toluene and D-pyridine) to enhance scattering contrast, there is always a need to check the effect of the deuterated component, the isotope effect. This was achieved by mixing protonated and deuterated solvents to see if the results will change—a technique known as contrast variation. Figure 5 shows a series of measurements using the mixed solvents. The scattering intensity spectra are similar except for their intensities because of the contrasts.

Knowing that the deuterated solvent effect is negligible, the next question will be the morphology of the aggregates. Obviously, the aggregate should be morphologically very different from a surfactant system because surfactant molecules can tightly pack into an aggregate while asphaltene molecules cannot. In asphaltene aggregates, it is expected to have voids because of the wide spread of the molecule structures. Reasonable questions to ask regarding the packing morphology are the roughness of the aggregate surface, the ‘core’ size and their void volume. One approach is by using the SANS contrast variation technique.

Figure 6 shows 5% asphaltene solutions in different environments. SI-A2H is a 5% asphaltene in 4:1 (by volume) mixture of protonated toluene and pH = 2 deuterated water.

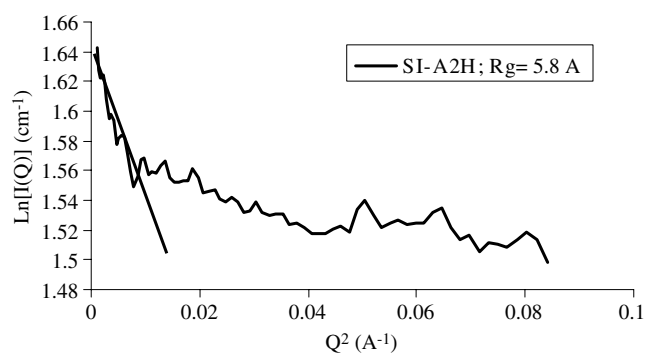


Figure 6. Contrast variation experiment. See the text for the composition and details.

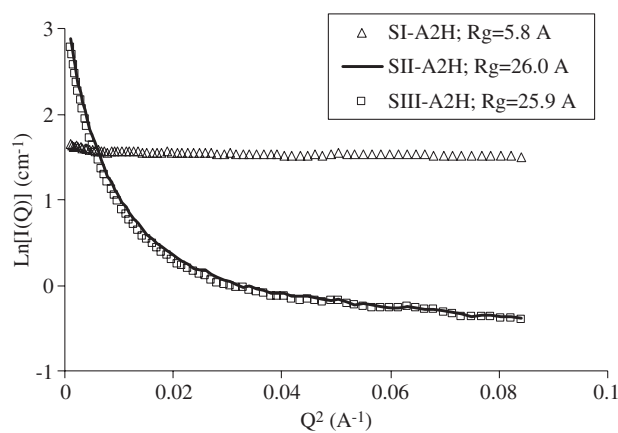


Figure 7. Contrast variation study with SI-A2H = asphaltene/H-toluene/D-water, SII-A2H = asphaltene/D-toluene/H-water and SIII-A2H = asphaltene/D-toluene/D-water.

Because the major structure is asphaltene aggregates but is ‘masked’ by the protonated toluene in the bulk, only the deuterated water region shows neutron scattering contrast with respect to the environment. Thus, the scattering is mainly from the water region. The ‘water core’ was found to be 5.8 Å in the radius of gyration, approximately one asphaltene molecule dimension. Note that the scattering intensity is very low.

The next two systems (figure 7) are SII-A2H, the same concentration and oil:water ratio but the toluene is deuterated and the water protonated, and SIII-A2H, deuterated toluene and deuterated water. As one can see the particle sizes extracted for SII-A2H and SIII-A2H are similar as expected. Physically, this means that the surfaces are not rough and it is hydrophobic in nature. This is to say that the cores are more polar for water molecules to remain, in order to minimize the water–toluene contact. SANS demonstrates its unique capability in ‘examining’ the core and surface morphology. Later, a similar strategy is applied to a vacuum residue instead of a solvent system and a similar conclusion can be drawn.

After studying the morphology, structures of aggregates, it is natural to ask the next question and that is how to prevent aggregation. One option is to introduce dispersant. If the dispersant successfully prevents aggregate formation we should see particle size being subdued. Here we investigated a simple surfactant, sodium dodecyl sulfate (SDS), and applied SANS to

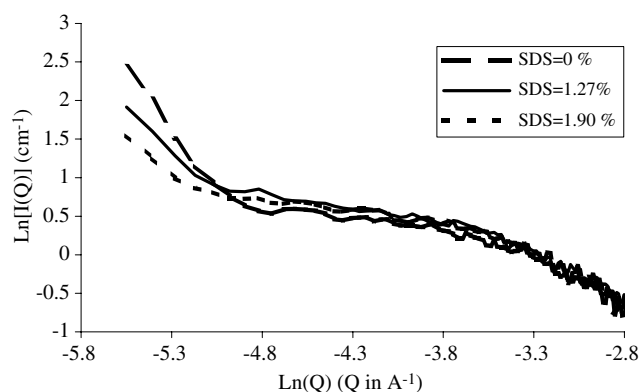


Figure 8. 5% asphaltene in toluene with added SDS.

evaluate the structural change before and after adding SDS. Figure 8 illustrates the scattering intensity distributions.

Apparently, SDS does have an effect on the structure of the aggregates. The striking point is that the effect is much greater on the low Q region than the high Q region. It clearly shows that the SDS does reduce clustering of the elemental particles but does not affect the structure of the elemental particles. This is a very important result. It suggests that the energy involved in the clustering of the elemental particles is much smaller and can be easily dispersed by adding a relatively weak dispersant like SDS. However, the elemental particles formed by the asphaltene molecules have much stronger aggregation energy, thus remain unchanged.

Having discussed the results from solvent systems, it is interesting to know if SANS can be applied to measuring asphaltene structure in vacuum residue with a small amount of deuterated solvent added. Figure 9 is such a study where different amounts of water were added to 5 wt% of Arabian medium heavy asphaltene/toluene solution. The scattering intensity distributions in the low Q range appear to be nearly unchanged. This means their elementary aggregate and the cluster (flocclants of the elementary aggregates) sizes remain unchanged. It indicates that water molecules prefer to reside in the core rather than with or between the clusters; otherwise, the particle sizes should increase. However, contrast in the higher Q range does increase drastically, making the incoherent scattering much smaller. This is a direct indication that water molecules are associated with the asphaltene core of the elementary aggregates. Moreover, the scattering intensity distribution functions are practically unchanged, meaning that the water molecules are filling the void of the elementary aggregates only. They do not change the status of the structure of the aggregates.

8. Discussion

Small angle scattering is a sophisticated technique with the obvious advantage that it is a true microscopic technique. Small angle scattering basically carries all the information we need to learn about a system, from microscopic to macroscopic properties. However, the scattering intensity distribution $I(Q)$ is an integrated quantity coupled by intra-particle (form factor) and inter-particle (structure factor) scattering spectra. In order to extract information one needs to de-couple $I(Q)$ into two factors. In the case of dilute asphaltene solutions, it is much less complicated. The interaction component is negligible and can be removed, leaving $P(Q)$, the form factor, the only function to deal with.

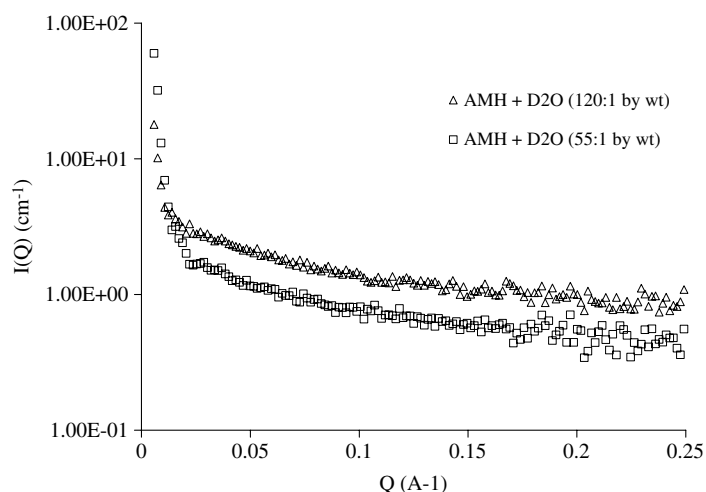


Figure 9. SANS of 5 wt% of vacuum residue derived Arabian medium heavy (AMH) asphaltene/toluene solutions with added deuterated water.

There are forward and backward methods to deal with $P(Q)$. The forward method is to presume the shape and compute $P(Q)$ to fit the data. This is a modelling approach, assuming a shape of the asphaltene particle. The drawback of this approach is obviously the modelling and the fitting process. Not only does one need to presume a particle size, shape and possible polydispersity distribution, the number of adjustable parameters in the fitting process may jeopardize the legitimacy of the extracted values. One way to avoid ambiguity is to obtain the absolute intensity, then perform fitting with restriction. Application of fitting restriction is non-trivial and can be misleading. In previous reports, we propose several methods to justify the fitting when the modelling approach is taken [16, 17].

The other approach is to apply model independent analyses. The simplest one is the Guinier plot. This approach is based on an assumption that the system is quasi-monodisperse. Moreover, it is only applicable in the Q range where QR_g is less than unity. However, the advantage of this approach is that it does not presume particle shape and R_g can be accurately determined. However, there are many systems with $QR_g > 1$, due to the limitation of instruments. In this case the Guinier analysis cannot be applied. Another case is when the system is polydisperse where an average R_g within a Q range may not include the particles that do not meet the $QR_g < 1$ requirement.

The other approach is the invariant method, which is related to the surface-to-volume (S/V) ratio. This approach has the obvious merit of being able to identify the particle shape more effectively. Its restriction is that integration of the scattering intensity data is necessary, in order to calculate S/V . In most cases, the data collected do not extend to large enough Q for the intensity to be close to zero. Error may arise and jeopardize the justification of the shape determined. In a previous work, we combined the modelling and the invariant method to identify particle shape and size [16].

The inverse Fourier transformation method is also applied to decouple the form factor and structure factor [9, 18]. Xu *et al* [21] applied this method to identify asphaltene aggregates as sphere-like. This is a good method but may suffer similar drawbacks to the S/V approach because Fourier transformation requires data to practically decay to zero for integration. In addition, if there is inhomogeneity in the system or within the scattering particles, this method will have to be abandoned.

Although model independent methods (i.e. without presuming particle shape) have several issues to deal with, it is still a much better method to use whenever possible. This is particularly important for asphaltene research because it is a mixture system and one expects some degree of inhomogeneity from one aggregate to the other. Therefore, it is more important to obtain a statistical average than to model an individual particle. In addition, most field applications require only the statistical parameters, which can be obtained using simple analysis. To this end, the requirements become more instrument related than data analysis related.

In this work, only Guinier analysis was used, yet it was sufficient to paint a good picture of the asphaltene aggregates, their clusters and the voids. This demonstrated that simply using an interpretation method is enough, but careful experimental design is needed in order to achieve quantitative assessment of a complex asphaltene system. This is a good demonstration of appropriate use of SANS and SAXS for complex systems.

9. Conclusion

Petroleomics requires a set of parameters to link to operational parameters. We proposed the colloidal length scale asphaltene aggregates be used as the basis for petroleomics. By combining SAXS and SANS and a series of coherent experimental designs we are able to unambiguously demonstrate that asphaltene molecules are of the order of 5–6 Å and the elementary aggregates about 30 Å. These aggregates do not increase in size upon increasing concentration but do cluster into much larger particles. The elementary aggregates consist of a large percentage of voids, measurable by the SANS contrast variation method. SANS and SAXS are vital tools for asphaltene aggregate characterization if petroleomics is to be established. It will be much more difficult to establish petroleomics if the structure and properties of the elementary aggregates and their propensity for further clustering cannot be accurately predicted from the seemingly very diverse molecular structures.

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