

NEUTRON SCATTERING CHARACTERIZATION OF ASPHALTENE PARTICLES

Min Y. Lin
Reactor Radiation Division, NIST, Gaithersburg, MD 20899
and
E.B. Sirota and H. Gang
Exxon Research and Engineering Co., Annandale, NJ 08801

Keywords: Asphaltene; particles; small angle neutron scattering

1. Introduction

The question of structure and association of asphaltene molecules in model solutions as well as in crude oils remains largely unanswered. It is however essential to the understanding of behavior of asphaltenes, specifically, their high viscosity. With small angle scattering techniques of neutrons and x-ray (SANS and SAXS), which probes length scales ranging from nanometers to near microns, it is possible to study the structure and aggregation behavior of asphaltene solutions, hence gaining the crucial information about their particle size, shape, physical interaction and phase behavior. Until recently, most such studies have concentrated on the basic asphaltene particles/micelles and their size, shape, while leaving larger size groups and long range correlations untouched, due to the difficulties of probing such long range length scales using SANS or SAXS. As a result, the high viscosity structure correlation of those solutions is still unclear.

In this work, we present first the conventional experimental data (momentum transfer $Q > 0.01 \text{ \AA}^{-1}$) obtained with SANS, which can be interpreted with a model of disk like shape for the basic asphaltene particles. These particles have an average radius of gyration around 40 \AA . Even though the size distribution is fairly polydisperse, most of the particles are below 100 \AA . At larger length scales ($Q < 0.01 \text{ \AA}^{-1}$), high resolution SANS data show that the scattering profile continue to rise, suggesting large length scale correlation or large particles present. While the large length scale correlation is the popular explanation, we try to interpret it as the signature of the presence of large particles. Unfortunately, those particles are so large that no scattering technique currently can probe their Guinier range to directly measure their size. Indirectly, we estimate their size based upon scaling arguments.

2. Basic Particles

Figure 1 shows a typical scattering intensity profile obtained from a dilute asphaltene solution with SANS. The intensity $I(Q)$ as a function of the momentum transfer Q is over a "conventional" small angle range, i.e., $0.006 < Q < 0.2 \text{ \AA}^{-1}$. In this range, the data can be fitted with a model for the particles with certain shape and size distribution. While no model is unique[1], we use a model of disk-shape and a Shultz distribution for the radius. Except at the lowest Q , the fitted curve shown in Fig. 1 is a good representative for the data. The fit results in an average radius (first moment of the radius distribution) $a = 14 \text{ \AA}$ with a standard deviation of $\sigma = 92\%$, and the thickness of the disk is $l = 20 \text{ \AA}$.

The radius distribution is shown in Fig. 2. As can be seen, the distribution is rather broad. Indeed, if one uses the first moment to calculate the radius of gyration of the disk, it is

$$\langle R_g \rangle_1 = (a^2/2 + l^2/3)^{1/2} = 11.5 \text{ \AA},$$

which is quite small compared to the radius of gyration $\langle R_g \rangle_G$ obtained in a Guinier fit for the same data which is close to 40 \AA . This is because that the Guinier fit represents a higher, different moment of the distribution.

The Shultz distribution has the following form: it is the product of a power law and an exponential decay:

$$P(r) = A r^{\alpha-1} \exp(-\beta r)$$

where $\alpha = 1/\sigma^2$, $\beta = \alpha/\langle r \rangle$, and A is a normalization constant. $\langle r \rangle$ is its first moment, and is typically used as the average. It can be shown that the n th moment is

$$\langle r^n \rangle = \langle r \rangle^n (\alpha+n-1) \dots (\alpha+2)(\alpha+1)/\alpha^n$$

The Guinier radius of gyration is obtained as

$$\langle R_g \rangle_G^2 = -3 \frac{\partial}{\partial(Q^2)} \ln I(Q \rightarrow 0) = \langle m^2 R_g^2 \rangle / \langle m^2 \rangle.$$

For the disk model, it is related to the 6th moment, and therefore is

$$\langle R_g \rangle^2 = \langle r^6 \rangle / 2 \langle r^4 \rangle + l/3 = 47.8 \text{ \AA},$$

which is more than 4 times larger than the first moment.

3. Large Size Particles

Even though the size distribution of the "basic" asphaltene particles are fairly broad, a typical particle size is well below 100 Å. The rheological property of the solutions can hardly be understood by the mere existence of these particles, if no further interaction or association of them is considered. However, in the Q range shown in Fig. 1, scattering intensity for concentration below 5% scales with the concentration, suggesting no interaction in the length scales probed[2]. The only interaction shown by SANS is the rise in intensity for $Q < 0.01 \text{ \AA}^{-1}$. Unfortunately, this has been largely ignored, mostly due to the limited range it is probed. However, it could be an important clue for the interaction or structure that is responsible for the macroscopic properties.

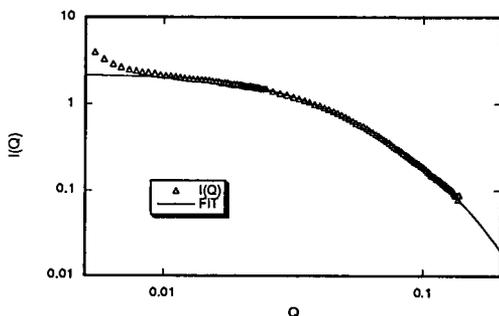


Fig. 1 SANS intensity as a function of Q. It was taken from a 2.5 wt% asphaltene (C7) solution in 1-methyl naphthalene-d10 at temperature 60 °C. The solid line is a fit with a disk-like particle shape. The distribution of the radius of the disk is shown in Fig. 2.

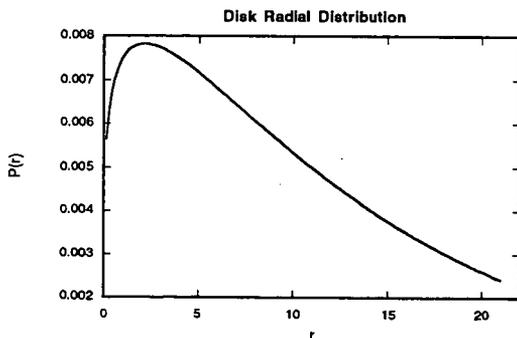


Fig. 2 Shultz distribution of the disk radius used to fit the data in Fig. 1. The average radius is $\langle r \rangle = 14 \text{ \AA}$, and standard deviation is $\sigma = 0.92$.

In Fig. 3, we show two SANS data sets taken to Q below 0.005 \AA^{-1} . In this extended Q range, the low- Q rise in intensity is more dominant. A quantitative analysis of the low- Q data in terms of the interactions of the basic particles is still difficult, although a fractal model has been proposed[3]. In our data, however, the slope shown at low Q is close to $s = -4$, the Porod slope, therefore it is not possible for a fractal structure (a mass fractal has $s > -3$, where $-s$ is the fractal dimension). On the other hand, a slope of -4 is typical for a compact object, in a Porod region of scattering intensity, much like those basic particles, which show a similar behavior, but at much larger Q ($Q > 0.1 \text{ \AA}^{-1}$), as shown also in the Figure. We can speculate that there are very large particles present in the solution, which could be compact aggregates of the basic, much smaller particles discussed above. However, the Guinier range of those large particles are in such a Q that is too small to measure by today's small angle scattering instruments. Light scattering would provide a right Q range, but the high absorption of light by those particles makes a light scattering measurement very difficult, if not impossible.

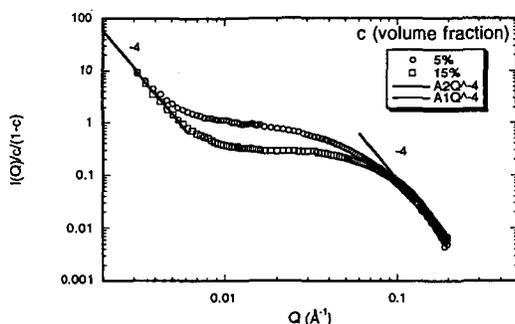


Fig. 3 SANS intensity normalized by the concentration for 5.0 wt% (circles) and 15 wt% (squares) in 1-methylnaphthalene-d10 at room temperature. At both lowest and highest Q ranges, the data show a -4 slope (Porod scattering).

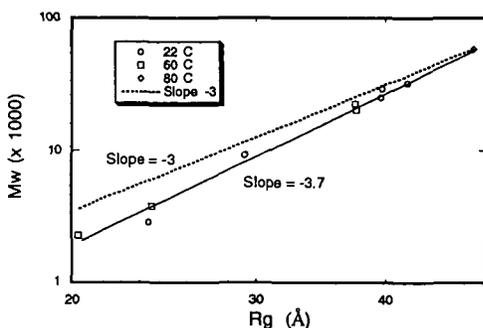


Fig. 4 Molecular weights and radii of gyration obtained from several solutions ranging from 0.5 wt% to 24 wt% at varying temperatures. Each point represents one solution at one temperature.

In Fig. 4, we plot the radius of gyration $\langle R_g \rangle_G$ as a function of its molecular weight M_w (particle mass multiplied by the Avogadro constant) of the basic particle obtained for several solutions at different temperatures. While both $\langle R_g \rangle_G$ and M_w are obtained from the same curve, they are actually independent. Although some of the solutions are higher than 5%, we assume that there are no interactions between the basic particles for both numbers to be meaningful. This assumption is related to, and consistent with the other assumption that the low Q behavior of the scattering is due to another group of particles with much larger sizes. Drawing a straight line through the points in the logarithmic plot, we find a slope of $s = 3.7$. Since $M \sim R^d$, where R and M are the size and mass of a particle, we should have $s = d$. The dimension d can never be larger than 3 in 3 dimension space where the asphaltene solutions are, unless the mass is not conserved.

This is actually consistent with the assumption that there are another group of mass present in the solution, and the total mass of the basic particles is indeed not conserved. It flows back and forth to the large size group, as conditions like concentration and temperature change. When concentration is increased or temperature lowered, there are more basic particles aggregated to form larger particles, resulting in a decrease of the total mass for the basic particles. If we assume both groups are compact particles ($d = 3$) as suggested by the slopes of -4 in Fig. 3, we can draw another line in the figure, with a slope of $s = d = 3$. The interception of the two lines is at a point taken from a 0.5 wt% solution at 80 C, where the low Q scattering is almost flat, suggesting no large size group present. The vertical distance between the two lines relative to the height of the upper line gives the percentage of mass missing from the smaller size group, and therefore is the percentage of mass residing in the large size group. Since we know the total concentration of the solution c , we then know from the graph c_1 and c_2 , the concentrations of each group, as $c = c_1 + c_2$, the total mass has to be conserved.

Furthermore, the amplitude of the intensity in a Porod region is proportional to both concentration c and S/V , where the surface to volume ratio for most low aspect ratio objects is in turn proportional to $1/R_g$, its size inversed. Thus for the two groups in the same solution under certain temperature, we have

$$\frac{A_1}{A_2} = \frac{c_1 R_{g2}}{c_2 R_{g1}}$$

$$\text{or } R_{g2} = \frac{A_1 c_2}{A_2 c_1} R_{g1}.$$

Since we know all the quantities on the right side, we can then calculate the larger size R_{g2} . For the 15 wt% solution, we obtain $R_{g2} = 9.7 \mu\text{m}$. The size is fairly large, and we need independent verification.

4. Conclusion

We present an analysis for asphaltene solution data obtained with SANS that suggest the presence of two distinctive groups of particles, vastly different in their sizes. The "basic" group, while smaller in size, is the majority when the solution is very dilute and temperature is high. Their typical size is about 40 Å and is readily seen by SANS and SAXS. For the other group, the size is larger than 1000 Å and therefore is hard to probe even by high resolution SANS or SAXS. They are mostly results of the aggregation of the smaller-size particles when concentration is high and temperature is low. From thermodynamic point of view, it is not totally unreasonable. However, many questions remain, e.g., one of which is why no particles in the intermediate size range exist.

This analysis is in contradiction to the conventional understanding that the low Q behavior of the scattering merely reflects the interactions among the basic particles. More recently we performed experiments before and after dilute solutions were filtered with sub-micron filters, partially confirming the results of our analysis.

References

1. E.Y. Sheu, and D.A. Storm, in E.Y. Sheu and O.C. Mullins (editors) *Asphaltenes, Fundamentals and Applications*, Plenum Press, New York, (1993).
2. M.Y. Lin et al, unpublished.
3. J. Briant, G. Hotier, *Revue de l'Institut Francais du Petrole*, **38**(1), 83 (1983); and Y.C. Liu, E.Y. Sheu, S.H. Chen and D.A. Storm, *Fuel* **74**, 1352 (1995).