

SMALL ANGLE X-RAY SCATTERING STUDY OF ASPHALTENES

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INTRODUCTION

Asphaltenes are molecules that can be precipitated from carbonaceous liquids by certain non-polar solvents¹⁻³. Traditionally they were those molecules in petroleum residuum that were soluble in benzene and insoluble in pentane, but over the years molecules precipitated by other solvents, usually heptane², and molecules precipitated from other materials, such as coal and oil shale liquids have been called asphaltenes³. As such there can be many kinds of asphaltenes, each a mixture of a number of molecules. In this work we have studied the heptane insolubles of vacuum residue from Ratawi crude oil.

Although petroleum asphaltenes have been studied for some time⁴, their physical nature, or macrostructure, in petroleum is poorly understood. Small angle X-ray scattering(SAXS) is a technique that can be used to study asphaltenes in their natural state. Early SAXS experiments confirmed the colloidal nature of crude oil^{5,6}, atmospheric residue⁷, and solid asphaltic materials⁸. Scattering centers were observed with radii of gyration in the range of 30-70 Å, indicating either the presence of macromolecules⁷, or micelle-

like particles.⁸ In more recent studies the authors have tried to obtain more information by fitting the observed scattering intensity with an intensity calculated for model particles.^{9,10} Senglet et al. however noted that polydispersity complicates the analysis.¹⁰ For example the well-known Guinier analysis failed in their study of asphaltenes in toluene, or gas oil.¹⁰ Applying a method suggested by Vonk¹¹, they extracted histograms for the radii of gyration that are quite broad.¹⁰ Recently Sheu¹² suggested some ambiguity can be removed by applying a constraint that follows from the assumption of homogeneous particles. Operationally we have:

$$I(Q) = A \langle F_0^2(Q; \text{shape, size}) \rangle \quad (1)$$

where $I(Q)$ is the measured scattering intensity, and $\langle F_0^2 \rangle$ is the normalized form factor for a particular particle shape and size distribution function. Equation (1) defines A , which also depends on the shape and size parameters used in the fitting. Since the scattering intensity is:

$$I(Q) = N(\Delta\rho)^2 V_p^2 \langle F_0^2 \rangle \quad (2)$$

for identical particles, where N is the number of particles per unit volume, $\Delta\rho$ is the contrast between particles and fluid, V_p is the particle volume and $\langle F_o^2 \rangle$ is the square of the normalized form factor averaged over orientation angles, we would expect for a polydispersed sample that:

$$\alpha - A(shape, size) / (N(size) \langle V^2(shape, size) \rangle \langle F_o^2(shape, size) \rangle) \quad (3)$$

is independent of the shape and size parameters for the right shape and distribution function, since Eq.(3) express the fact that the contrast is constant for homogeneous particles. The constraint is applied by requiring that Eq.(3) remain constant as the concentration is varied; i.e., the parameters of the distribution may change, but the form of the distribution function, and the particle shape can not change. This procedure was used to fit the scattering data obtained with natural and synthetic Ratawi vacuum residue. The asphaltenic particle sizes (radii) are distributed according to a Schultz distribution. The average radius agree well with the radii of gyration reported earlier⁵⁻⁸, and the spherical shape agrees with the recent rheological studies for Ratawi asphaltenes in vacuum residue¹³, and in toluene.¹⁴

EXPERIMENTAL

Ratawi crude oil comes from the Neutral Zone in the Middle East. The vacuum residue was obtained by vacuum distillation; it is the fraction that has an apparent boiling point above 1000 °F. Samples of synthetic vacuum residue were prepared by dispersing appropriate amounts of vacuum residue in the corresponding non-asphaltenic portion. The non-asphaltenic fraction was prepared by first mixing heptane with the vacuum residue in the ratio of 40 parts of heptane for each part of vacuum residue, then stirring overnight at room temperature, and finally removing the asphaltenes by filtration. Heptane was removed from the non-asphaltenic portion by vacuum distillation.

The SAXS measurements were made with the ten meter small angle scattering spectrometer at Oak Ridge National Laboratory. The X-ray generator was a Rigaku-Demki rotating anode with a copper target; the power was 4KW. The K_{α} wavelength of 1.54 Å was selected using a pyrolytic graphite monochromator. The input collimator and a series of pinholes produced a 1 mm² spot at the sample position. The sample to detector distance was 112.6 cm. The detector was a 20 x 20 cm² continuously wired area detector purged by P10 gas. With this configuration the scattering wave vector Q ranged from 0.1 to 0.25 Å⁻¹. The samples were heated to 125 °C and then injected into a Kapton sandwich circular cell with a path length of 1 mm. The temperature was maintained at 93 °C during the experiment. Scattering from empty cells with and without Kapton windows was also measured for subsequent use during data reduction. A

calibrated polyethylene standard of known cross section at the peak position was used to obtain the absolute intensity (differential cross section per unit volume of sample)

RESULTS AND DISCUSSION

As discussed above, the measured scattering intensities were fit according to the procedure suggested by Sheu.¹² The fit obtained for spherical particles with sizes distributed according to the Schultz distribution for the Ratawi vacuum residue is shown in Figure 1. Other particle shapes and distributions were tried, but the alpha values defined in Eq.(3) were not constant. For example, the data for a particular sample could be fit by monodispersed cylinders, but the alpha values were not constant as the concentration was changed.

The Schultz distribution functions is shown in Figure 2. The Schultz distribution is defined as follows:

$$D(R) = [(z+1)/\langle R \rangle]^{z+1} R^z e^{-(z+1)R/\langle R \rangle} / \Gamma(z+1)$$

where $\langle R \rangle$ is the average radius, $\Gamma(z+1)$ is the gamma function, and z is a width parameter related to the polydispersity as

follows:

$$\text{polydispersity} = \sqrt{(\overline{R^2}) - (\overline{R})^2} / (\overline{R}) = 1/\sqrt{z+1}$$

The average radius and the degree of polydispersity is 33.8 Å and 15.4%. There are particles with radii as small as 20 Å and as large as 50 Å in this distribution. The average radius agrees very well with the radii of gyration reported by others for crude oil^{5,6}, atmospheric residue⁷, asphaltic materials⁸, and asphaltenes in solvents.⁵⁻⁸ The distributions are broad, as also found by Senglet et al.¹⁰ using the method due to Vonk.¹¹ The spherical shape for the asphaltenic particles is in agreement with the rheological measurements for these asphaltenes in vacuum residue¹³ and in toluene.¹⁴

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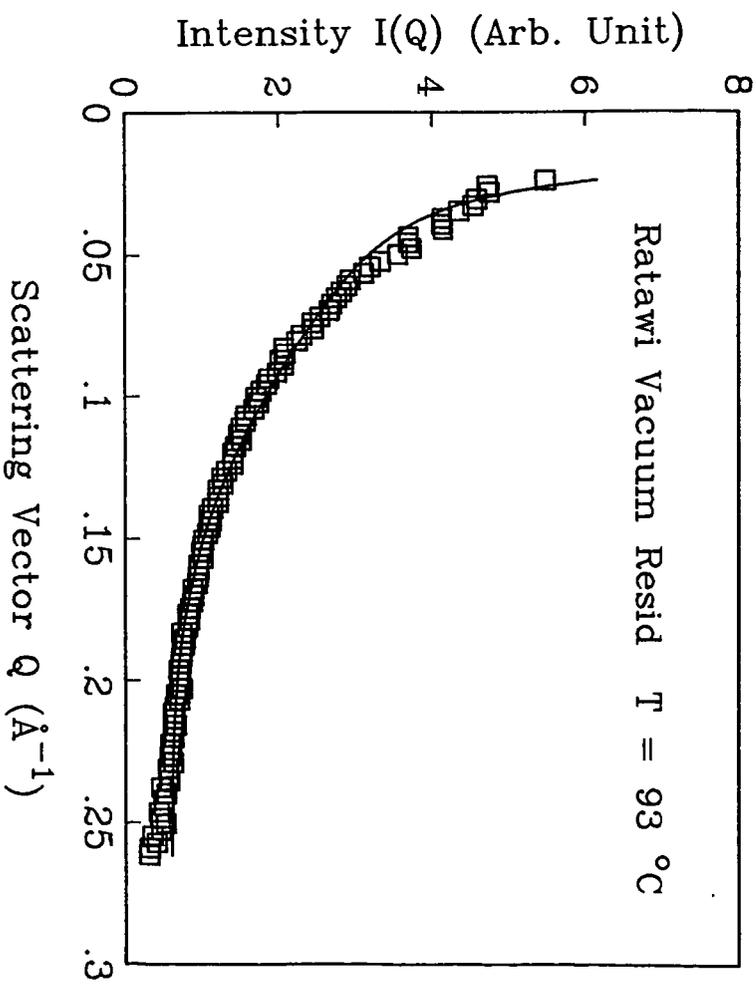
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FIGURE CAPTIONS

Figure 1 Scattering intensity for Ratawi vacuum residue at 93° C

Figure 2 Distribution of radii of asphaltenic particles



Particle Size Distribution

