Characterization of Asphaltene Micelles and Their Interaction in Vacuum Residue of Crude Oil by Small-Angle Neutron Scattering

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Experimental study on the micellar structure of asphaltenes and their interaction in Arabian heavy vacuum residue (AH-VR) was performed utilizing small-angle neutron scattering (SANS) technique. Since asphaltenes are mainly composed of poly-condensed aromatics, they intend to form micelles in the heavy oils, and they strongly affects the physical and chemical properties of heavy oils. Based on the analysis of SANS, we established the precise micellar structure of asphaltene.

KEYWORDS: small-angle neutron scattering, asphaltene micelles, crude oil, micellar structure

§1. Introduction

Recently, the development of better refining technology of heavy oil is becoming more important in the field of oil industry, because available crude oils become heavier and more concentrated in sulfur and metals.[1,2] Asphaltene, which is the n-heptane insoluble fraction of petroleum, strongly affects the property of crude oil, though its content is slightly several percent in weight. Asphaltenes are composed of poly-condensed aromatics, they intend to form micelles in the heavy oils by interacting each other and strongly affect the physical and chemical properties of heavy oils. It is, therefore, very important to clarify the precise micellar structure of asphaltene in order to design the catalysts for upgrading of the heavy oil. Many experiments were performed on the asphaltene using many analytical methods,[3–6] but the precise structure, specially internal structure within the micelle, had not be clarified yet. In this study, we carried out the experimental study on the micellar structure of asphaltenes in Arabian heavy vacuum residue utilizing small-angle neutron scattering (SANS) to make clear the precise structure of asphaltene micelles.

§2. Experimental

Samples used were Arabian Heavy Vacuum Residue (AH-VR) and VR fractions (b.p.=520 °C) of the hydrotreated oil from AH atmospheric residue (b.p.=343 °C). Asphaltene was prepared from VR with addition of n-heptane. Hydrotreatment was performed in a fixed bed continuos flow reactor system,[7] in which hydrodemetallization (HDM) and hydrodesulfurization (HDS) catalysts were installed, respectively. Both reactions were performed at 380 °C under the condition of 12 MPa of reacting hydrogen gas. The ratio of oil and hydrogen was 1:800.

SANS was measured by placing the sample cell of ultra pure aluminum as a function of the concentration (0.5 wt%, 1.0 wt%, 2.0 wt%) of asphaltene and the temperature (13 °C, 100 °C, 200 °C, 250 °C) which was conducted by a thermo-controller. A deuterated toluene was used as a solvent. The thickness of sample in which neutrons passed was 4mm. The accessible q range ($q = 4\pi\sin(\theta)/\lambda$, where λ is the wavelength of probing neutrons and θ is half the scattering angle) was 0.04 to 2.00 nm^{-1}. The experiment was performed at the JRR-3 of Japan Atomic Energy Research Institute.

§3. Results and Discussion

Figure 1 shows the typical $itq - I(itq)$ plots of asphaltene micelles of AH-VR, AH-HDM, AH-HDS at room temperature in the case of the concentration was set to1.0wt%. AH-VR and AH-HDM were measured twice for evaluating the reproducibility.

The analysis of the neutron scattering data to obtain the size information can be made by using the Guinier approximation ($I(q) = I(0) \exp(-q^2 R_G{}^2/3)$, where $I(0)$ is the intensity at $q = 0$). Guinier radius (R_G) of AH-VR, HDM and HDS calculated based on the SANS measurements for Guinier region ($0.3 \leq q(1/nm) \leq 1.1$) are summarized in Table I. The concentration was set at from 0.5 wt% to 2.0 wt%. As shown in the table, there existed no concentration dependency on R_G in each species, but both R_G of HDM and HDS were much larger than that of VR. The results apparently suggest the existence of molecular association of asphalten micelles by hydrodemetallization process.

Table II shows the dependence of the temperature on the R_G of AH 2.0 wt% d-toluene solution. It was obvious that R_G become smaller at high temperature region, even though the R_G of AH did not have the concentration dependence in our experiments. R_G obtained by the measurement shows that the size of asphaltene micelle at 250 °C was just half compared with that at room temperature, and R_G was rapidly changed over 200 °C.
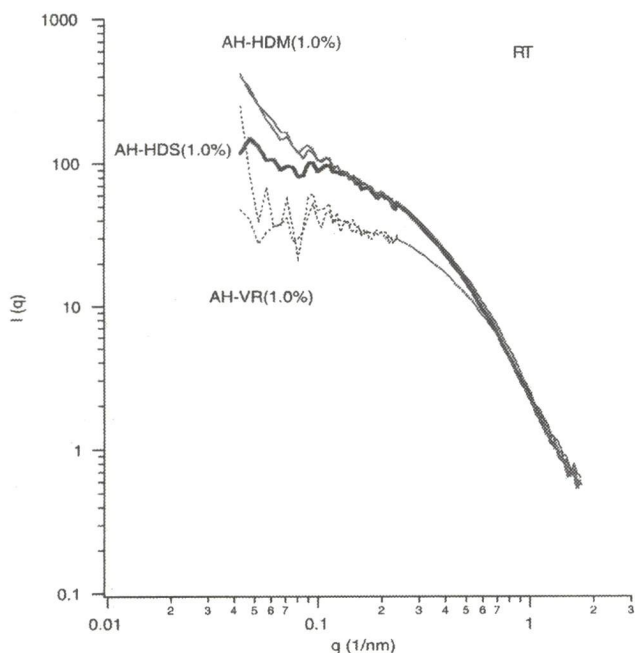
Fig. 1. q-I(q) plots of asphaltene micelles of Arabian Heavy Vacuum Residue (AH-VR), hydrodemetallization (AH-HDM) and hydrodesulfurization (AH-HDS) of 1.0 wt% d-toluene solution at room temperatute.

Table I. R_G of asphaltene micelles at room temperature.

	Concentration (%)	R_G (nm)
AH-VR	2.0	3.728
	1.0	3.730
	0.5	3.666
AH-HDM	2.0	4.428
	1.0	4.417
	0.5	4.332
AH-HDS	2.0	4.494
	1.0	4.513
	0.5	4.468

Table II. R_G of Asphaltene micelles of AH 2 wt% d-toluene solution as a function of temperature.

Temperature (°C)	R_G (nm)
23	3.67
100	3.06
200	2.76
250	1.94

Therefore it needs high temperature condition more than about 200 °C to dissolve the asphaltene micelles.

The intensity of neutron scattering spectrum is the following,

$$\frac{d\Sigma(q)}{dq} = I(0)P(q)S'(q) \qquad (3.1)$$

where $P(q)$ is a form factor, and $S'(q)$ is the structure factor which describes the interparticle effect. In our analysis, $S'(q)$ is assumed to be 1, because we deal with the domeins in the high q region, in which a form factor
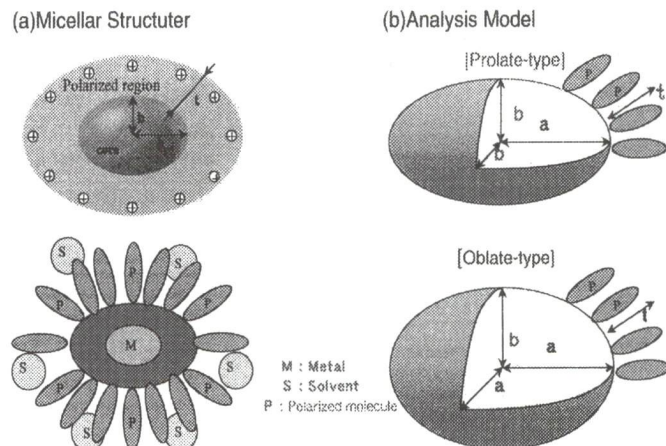

Fig. 2. Micellar structure (a) and analysis model (b) of asphaltene. M, S and P mean Metal, Solvent and Polarized molecule, respectively. a, b and t are geometric parameters of micelle.

is dominant compared with interparticle factor .

We set the analytical model shown in Fig. 2. As for $I(0)$, it was estimated by the SANS measurement of standard material. Asphalten micelle has the core region and the polarized region around it. We considered two types of micellar structures, which were the prolate-type and the oblate-type. The sphere structure is a special case in both models.

As for the micelle models shown in Fig. 2, the form factor was derived as below,[8)]

$$P(q) = \int_0^1 bF(q,\mu)b^2 d\mu \qquad (3.2)$$

$$F(q,\mu) = x\frac{3(sin(qR_1) - qR_1cos(qR_1))}{(qR_1)^3}$$
$$+(1-x)\frac{3(sin(qR_2) - qR_2cos(qR_2))}{(qR_2)^3} \qquad (3.3)$$

$$x = \frac{(\rho_p - \rho_c)V_c}{(\rho_p - \rho_c)V_c + (\rho_s - \rho_p)V_m} \qquad (3.4)$$

where μ is the cosine between q and b axis defined in Fig.2, and ρ is the scattering length (c, p and s mean core, polarized region and solvent, respectively). R_1 and R_2 are derived according to the structure of micelles, as are shown below,

Prolate type :

$$R_1 = [a^2\mu^2 + b^2(1 - \mu^2)]^{1/2} \qquad (3.5)$$

$$R_2 = [(a + t)^2\mu^2 + (b + t)^2(1 - \mu^2)]^{1/2} \qquad (3.6)$$

$$V_c = \frac{4\pi}{3}ab^2 \qquad (3.7)$$

$$V_m = \frac{4\pi}{3}(a + t)(b + t)^2 \qquad (3.8)$$

Oblate type :

$$R_1 = [a^2(1 - \mu^2) + b^2\mu^2]^{1/2} \qquad (3.9)$$

$$R_2 = [(a + t)^2(1 - \mu)^2 + (b + t)^2\mu^2]^{1/2} \qquad (3.10)$$

$$V_c = \frac{4\pi}{3}a^2b \qquad (3.11)$$

$$V_m = \frac{4\pi}{3}(a+t)^2(b+t) \qquad (3.12)$$

We tried to fit the $d\Sigma(q)/dq$ by operating the structure parameters utilizing equations discussed above, but any attempts were not succeed as far as using the oblate-type model. Fig. 3 shows the $d\Sigma(q)/dq$ at $q=0.1(1/\text{Å})$ as a function of $a(\text{Å})$ and $b(\text{Å})$ in the oblate model. $t(\text{Å})$ was derived by taking into consideration of R_G. Though the experimental value of $d\Sigma(q)/dq$ at $q=0.1(1/\text{Å})$ is 0.3 (1/cm), Fig. 3 shows that the $d\Sigma(q)/dq$ was always less than 0.2 (1/cm) at any condition.
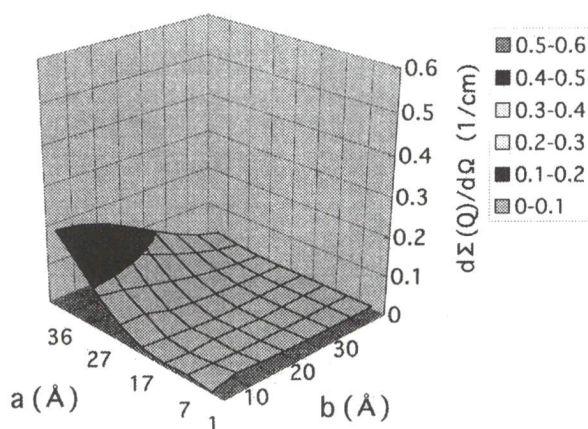
Fig. 3. $d\Sigma(q)/dq$ at $q=0.1(1/\text{Å})$ as a function of $a(\text{Å})$ and $b(\text{Å})$ in the oblate model.

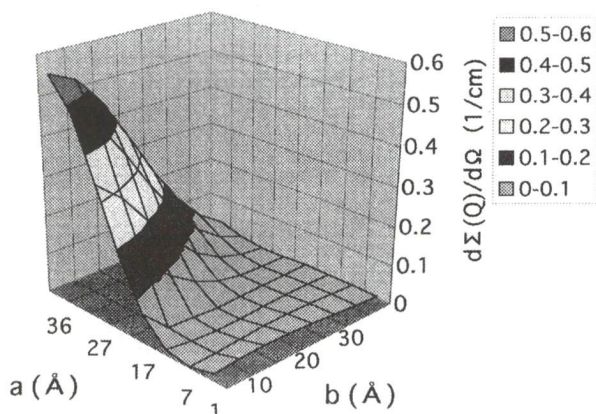Fig. 4. $d\Sigma(q)/dq$ at $q=0.1(1/\text{Å})$ as a function of $a(\text{Å})$ and $b(\text{Å})$ in the prolate model.

The $d\Sigma(q)/dq$ of the prolate type is shown in Fig. 4. From the figure, $d\Sigma(q)/dq$ had a value of 0.3 (1/cm) in some suitable conditions. In the prolate-type model, we could succeed in fitting the spectrum pattern (Fig. 5).

Based on the precise analysis of SANS of AH-VR, as was mentioned before, we found that the micelle had prolate-type with $a=29$ Å, $b=7$ Å, and the thickness of polar region of micelle was 8 Å. Then the smallest diameter of asphaltene micelle was 30 Å$(=2(b+t))$. The accuracy of the fitting parameters is about $\pm 1\text{Å}$. In general, the maximum pore size of FCC (Fluid Catalytic Cracking) catalyst is about several Å, therefore the results led us to suggest that the new type catalyst that
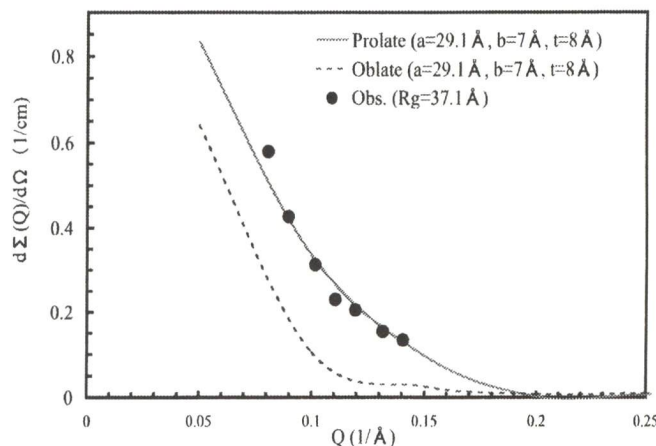

Fig. 5.   Curve fitting of the scattering intensity $(d\Sigma(q)/dq)$ of AH-VR using the prolate model and the oblate model.

should have more large pore size was needed to disolve the asphartene micelles.

§4.   Conclusions

Experimental study on the micellar structure of asphaltenes in Arabian heavy vacuum residue was performed utilizing small-angle neutron scattering (SANS). We clarified the precise micellar structure of asphaltene in AH for the first time. Based on the analysis of SANS, we found that the core of micelle had the prolate structure of $a=29$ Å, $b=7$ Åand that the thickness (t) of polar region around the core was 8 Å. SANS is indeed a very powerful tool to understand the micellar structure of asphaltenes. The precise evaluation of the effects of hydrodemetallization and hydrodesulfurization will be reported elsewhere.

Acknowledgements

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