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Study on mixing scheme and fluctuation of an aggregate in a heavy oil

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1 Introduction

Asphaltene is the heaviest fraction which consists of high molecular weight aromatic compounds, existing as aggregates in petroleum. It is important to clarify the asphaltene aggregation behavior at high temperature in organic solvent, because the aggregation causes catalyst deactivation in refinery process.

To examine the aggregation behavior of asphaltene at high-pressure and high-temperature conditions in toluene, small-angle X-ray scattering (SAXS) measurements with synchrotron radiation were conducted.

2 Experimental

At BL-6A, SAXS measurements for asphaltene-toluene mixture were performed along an isobaric at 10 MPa and temperatures up to 300 °C. The concentration of asphaltene is 5000 mg/L. An X-ray beam was monochromatized to λ = 1.50 Å and the observable s-region was 0.024 to 0.18 Å^{-1}, where the scattering parameter, s, is defined as $4\pi\sin\theta/\lambda$ (2θ : scattering angle, λ : wavelength).

For the SAXS measurement under high-pressure and high-temperature conditions, a sample holder was newly designed. The body is entirely made of titanium alloy (Ti-6Al-4V), which has relatively low thermal expansion and high resistivity against corrosion under extreme condition. Two diamond disks, 5.0 mm in diameter and 0.8 mm in thickness, were used as X-ray windows, and they were sealed with gold O-rings. Two cartridge heaters were inserted into the cell body. Temperature and pressure of the sample were measured using a thermocouple and a strain gauge, respectively.

3 Results and Discussion

Figure 1 shows the observed SAXS profiles, $I(s)$, of asphaltene at various conditions. All the SAXS intensities increase with the decrease of s. The degree of intensity increase at 29 °C is larger than those at higher temperatures, suggesting that the degree of asphaltene aggregation is the highest at lowest temperature.

Figure 2 shows the radius of gyration, R_g, which are obtained by the Zimm plot ($1/I(s)$ vs s^2) [1]. The values of R_g decrease from 5.1 to 3.9 nm with increasing temperature at lower than 200 °C, corresponding to the disaggregation of asphaltene structure by thermal energy. The R_g increase 3.9 to 4.4 nm at 200 to 300 °C. The increase of R_g at higher temperatures may come from the following mechanism: asphaltene swelling with high-temperature toluene which makes the size of aggregate larger, and/or solvent clustering which increases the apparent scattering volume due to "local density enhancement" around the scatter. The latter phenomenon is one of the unique properties of supercritical fluid [2].

4 Summary

SAXS profiles of asphaltene-toluene mixture at lower than 300 °C and 10 MPa were obtained to clarify the disaggregation behavior of asphaltene in organic solvent. It was suggested that the disaggregation of asphaltene was mainly observed up to 200 °C.

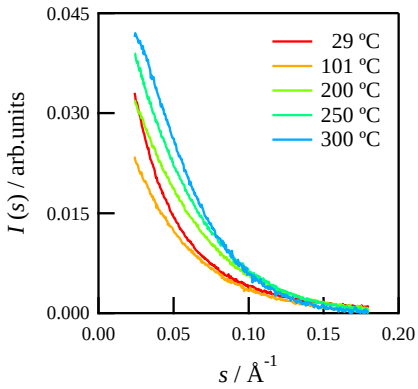

Figure 1. Temperature dependence of SAXS profiles of asphaltene in toluene.

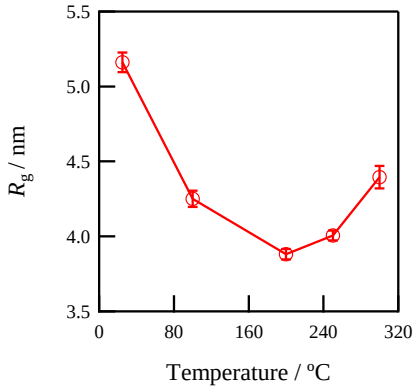

Figure 2. Temperature dependence of the radius of gyration, R_g, of asphaltene in toluene.

References

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