

STUDY ON THE MICELLE SIZE OF ASPHALTENES IN VACUUM RESIDUE BY DIELECTRIC LOSS

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KEYWORDS: asphaltene, micelle size, dielectric loss

INTRODUCTION

Asphaltene contained in heavy oils, such as crude oil or vacuum residue is obtained usually as the precipitates when adding alkane to heavy oil. It is defined as n-heptane insoluble-toluene soluble, for example. As asphaltenes are mainly composed of poly-condensed aromatics, they intend to form micelles in the oils by interacting each other, and their stacking governs physical and chemical properties of asphaltene rich heavy oils. A number of analyses have been made by using various kinds of measurements and micellar structural models have been proposed [1,2]. The size of micelle has been studied by using many techniques, such as X-ray diffraction (XRD), dielectric relaxation, rheological measurements, small angle neutron scattering (SANS) technique, X-ray absorption near edge structure (XANES) [3,4]. XRD was done for asphaltene powder, and the others were in various solvents. Therefore, it would not be clear the substantial size of micelles in the real heavy oil. During the course of characterization of asphaltene derived from Arabian heavy vacuum residue (AH-VR), we have found that the mass distribution was in the range from $m/z=200$ to 6000, having a broad peak near 1500 with a shoulder peak near 400, by means of laser desorption mass spectroscopy (LDMS) [5]. In this study, we have attempted to measure the dielectric response for AH-VR by an impedance analyzer, and found the loss peak due to asphaltene component. From the results about the effect on the concentration of asphaltene and resin in VR, the mechanism of micelle formation and the size of micelles are discussed.

EXPERIMENTAL

Samples used were AH-VR and VR fractions (b.p. of 793°K) of the hydrotreated oil from AH atmospheric residue (616°K). Asphaltene was prepared from VR with addition of n-heptane (solvent and VR ratio was 1g / 30ml). Maltene (n-heptane soluble) was separated to three fractions (i.e. saturate, aromatic and resin) by column chromatography. Hydrotreatment was performed in a fixed bed continuous flow reactor system, in which hydrometallization (HDM) and hydrodesulfurization (HDS) catalysts were installed respectively. The reactor system and reaction conditions were the same described previously except catalyst and LHSV of 0.75 hr⁻¹ [5].

Dielectric loss was measured with a Hewlett-Packard Impedance Analyzer (HP4194A), connecting with Liquid Test Fixture (HP16452A) at 403K. Electrodes with diameter of 38 mm each have been kept space of 1 mm. The working frequency range was from 100 Hz to 15 MHz. Viscosity measurement was made using a TOKIMEC B type viscometer.

RESULTS AND DISCUSSION

In a condenser of parallel plates, the dielectric loss (ϵ'') is represented as follows:

$$\epsilon'' = 1/2 \pi f C v R p \quad (1)$$

where f is the frequency, Cv the capacity in vacuum ($= \epsilon_0 A/d$), Rp the impedance, d the distance between electrode plates, ϵ_0 the dielectric constant of vacuum, and A the area of electrode [6]. As the conductivity (ρ) is equal to d/RpA , eq.(1) becomes:

$$\epsilon'' = \rho / 2 \pi f \epsilon_0 \quad (2)$$

In our results, the values of ρ at range from 10^2 to 10^3 Hz were rather small than those of higher frequency. So, we evaluated the difference dielectric loss ($\Delta \epsilon''$) calculated the following equation:

$$\Delta \epsilon'' = (\rho - \rho_{100}) / 2 \pi f \epsilon_0 \quad (3)$$

where ρ_{100} is the ρ at 100 Hz.

The dielectric loss spectra for AH-VR and fractions derived from it are shown in Figure 1. For AH-VR two peaks were observed at the low frequency side (7.94×10^2 Hz) and the high side (3.98×10^6 Hz), which were appeared due to the existence of the dipole. As the high frequency peak was also observed for maltene, the low frequency peak was contributed from asphaltene. The loss spectra for saturate and aromatic were also shown in Figure 1 (The spectrum for resin was not obtained because of its poor fusibility). Dielectric loss curve for the saturate was almost flat, while the one for aromatic showed a clear peak at about 3.98×10^6 Hz. The dielectric loss curve for resin would not behave any particular peaks. This is due to that the resin fraction is defined as the difference of maltene and the sum of saturate + aromatic. Dielectric loss spectrum for the resin, which has more or less polarity, was broad without any particular peaks. The relation between a dielectric relaxation frequency and a rotation radius is known as Stokes-Einstein equation:

$$f = k_B T / 4 \pi \eta R_d^3 \quad (4)$$

where k_B is the Boltzmann constant, T the temperature, η the effective viscosity, and R_d the dipole moment weighted particle radius [7]. According to eq.(4), the dipole radius of asphaltene was calculated, that is 10.4 nm.

In order to built up the molecular structure of the asphaltene; we have provided the following characterization parameters: Mw (by LDMS)=2040, carbon aromaticity, f_a (by $^1\text{H-NMR}$)=0.52. Structural parameters of the asphaltene molecules were calculated by a computer aided structure analysis method [8], and average structure model was drawn, where we were taking consideration the fact that the LDMS result suggested cata type of aromatic condensed ring in shape [5]. The longitudinal size of the asphaltene molecule was about 6 nm, which was about a half of the micelle radius obtained above. This is reasonable value from the mechanism of stacking of asphaltene molecules, because they interact each other by their polarity of aromatic sheets and/or metallic ions.

Figure 2 shows the dielectric loss curves for the mixtures of asphaltene with maltene. When the asphaltene content increased from 15.3 wt% (corresponding to the composition of VR) to 20 wt%, the loss peak became larger and shifted to the lower frequency side. On the other hand, the peak became smaller and shifted to the higher side for the mixture with 5 wt% of asphaltene. It was noticeable that the peak shape was rather flat in the case of 10 wt%, which might show the uncontinuous change in size. These evidences imply that the shape of dielectric loss spectra depend upon the content of asphaltene. It has been investigated the surface and interfacial tensions system for asphaltenes in aromatic solvents and indicated possible asphaltene aggregation as well as the probable existence of critical micelle concentration [2,9]. From the frequency at the maximum intensity of dielectric loss, we can calculate the micelle size in medium. The micelle radius for 5 wt% of asphaltene content is 8.4 nm, 9.7 nm for 10 wt%, 10.4 nm for 15.3 wt% (as shown above) and 10.4 nm for 20 wt%, respectively. It is suggested a critical micelle formation point at the given asphaltene concentration, which is below 5 wt% in our case.

The spectra changes of resin content in VR matrix are shown in Figure 3. The

frequency at the maximum loss were almost unchanged at the range from 23 wt% (corresponding to VR) to 0 wt% of resin content in matrix as well as the viscosity of the same specimens. The facts suggest the size of micelles might be independent on resin content. The intensity changes would be caused by the change of relative content.

Further, we have obtained dielectric property for VR fractions derived from hydrotreated oils with HDM and HDS catalysts. Characterization data were illustrated in Table 1, where asphaltene content decreased from 15.3 wt% in the original VR to 7.6 and 5.7 wt%, respectively. Although molecular weight distribution by LDMS for HDM and HDS shifted slightly to lower side, averages molecular weight was almost unchanged. Chemical structure expressed with f_a altered some extent with the hydrotreatment. In fact, structural parameters, such as the number of aromatic carbon, C_a , and the number of aromatic ring, R_a , were decreased by the hydrotreatment; C_a : 109 to 79 for HDM and 85 for HDS, R_a : 28 to 22 for HDM and 25 for HDS, respectively. Figure 4 shows the dielectric loss spectra for those VRs. The intensities for both samples decreased to the same extent and the shape was almost the same too. It is not clear why the shape of dielectric loss spectra did not change nevertheless decreasing the asphaltene content. From the results that metal content decreased from 121 ppm in the original VR to 66 and 31 ppm by HDM and HDS, respectively, it seems that the aromatic structure would be more effective on the intensity than metal. The loss spectra for these VRs became flat and the peaks were resultantly collapsing with the hydrotreatment, which was almost similar to that of 10 wt% of asphaltene as already illustrated in Figure 2. The micelle radii were calculated from the shoulder peak frequencies for reference, 9.3 nm of HDM and 10 nm of HDS, respectively. It would be suggested that the critical micelle formation point is deeply dependent upon the structural changes.

CONCLUSIONS

The micelle size of the asphaltene in Arabian heavy vacuum residue was investigated from the dielectric loss measurements at 403K. It was observed that the loss spectrum of asphaltene in AH-VR was in the wide range from 1×10^2 to 1.5×10^7 Hz having two peaks, and that the former was at low frequency and the latter was at high frequency. We found that the low frequency peak was contributed from asphaltene by comparing with that of maltene. The micelle size in VR was determined from the frequency at the maximum intensity of the loss spectra and the viscosity, using Einstein-Stokes equation, 10.4 nm in radius. This value was about two times of the length of the average molecular structure drawn from its characterization.

From the results of loss spectra changes with asphaltene and resin contents in maltene, and those for VR derived from the hydrotreated oils, it was found that the intensity of loss spectra was affected by not only asphaltene but also metal contents. And, it was also suggested that the aromatic structure would be more effective than metal.

Then, we discussed about the size of micelles determined from the loss spectra to make sure the mechanism of micelle formation. It was suggested that the micelle size might be depend upon the asphaltene content and the size of condensed aromatic rings of asphaltene, not upon the resin content, which implied the critical micelle formation point.

ACKNOWLEDGMENTS

This work has been carried out as a research project of the Petroleum Energy Center with the subsidy of the Ministry of International Trade and Industry.

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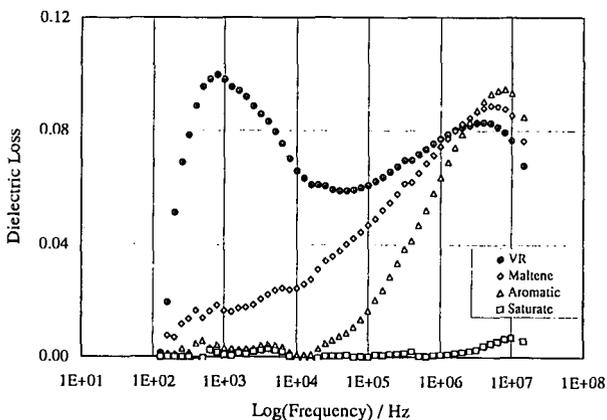


Figure 1. Dielectric loss spectra for AH-VR and fractions derived from it

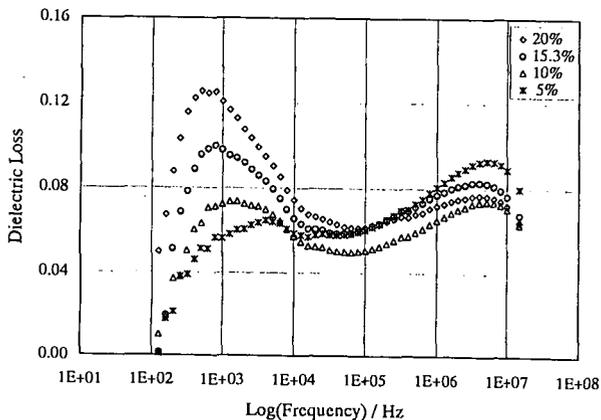


Figure 2. Dielectric loss spectra for mixture of asphaltene and maltene

Table 1. Properties of asphaltenes

Sample	Asph. Content Density		H/C	Mw	fa	Ca	Ra
	wt%	g/cm ³					
AH-VR	15.3	1.165	1.05	2040	0.52	109	28
HDM	7.6	1.180	1.07	2140	0.48	79	22
HDS	5.7	1.141	1.04	2130	0.54	85	25

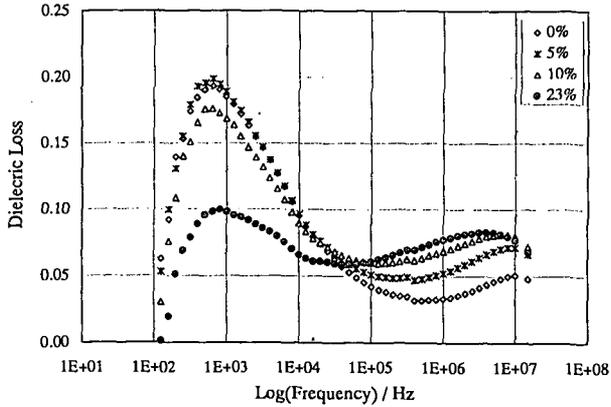


Figure 3. Dielectric loss spectra for mixture of resin and matrix

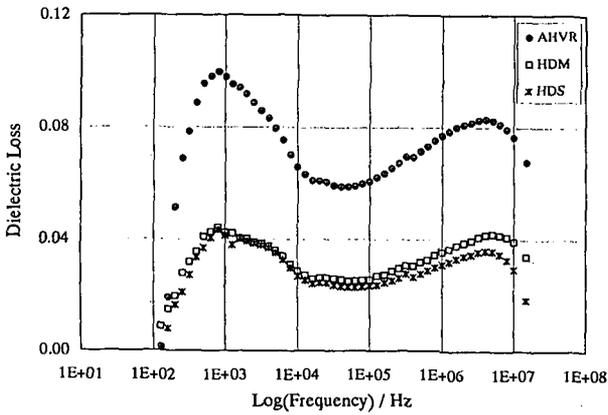


Figure 4. Dielectric loss spectra for VR obtained with hydrotreatment