Probing asphaltene aggregation in native crude oils with low-field NMR

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Recently, much progress has been made in elucidating the molecular and colloidal properties of asphaltenes. Many of the previous measurements of the sizes of asphaltene molecules and nanoaggregates have been made in model systems. When the asphaltenes are in their native crude oils, it is much more difficult to determine the size and configuration of the asphaltene particles, in part because of the complexity of the maltene and because of the optical opacity of the samples. Low field NMR relaxometry is well suited for measuring asphaltene properties within crude oils because it is sensitive to fluctuations at the Larmor frequency. For low field NMR operated at a few MHz, these time scales are in the range expected for the rotational correlation times of aggregates with sizes of a few nanometers.

In this presentation, we show that low field proton nuclear magnetic resonance relaxation and diffusion experiments can be used to study asphaltene aggregation directly in crude oils. The low field measurements are sensitive only to the maltene because the spins on the asphaltene relax too quickly to be detected. However, the asphaltene aggregation state can still be probed with this method because the maltene molecules' interactions with the asphaltene particles in the oil affects the relaxation of the spins in the maltene molecules. The NMR relaxation was found to be multiexponential as expected in a complex fluid. Remarkably, the relaxation data for samples with different asphaltene concentrations can be collapsed onto each other by simple rescaling of the time dimension with a concentration-dependent factor ξ, while the observed diffusion behavior is unaffected by asphaltene concentration. We interpret this finding in terms of a theoretical model that explains the enhanced relaxation by transitory entrainment of solvent hydrocarbons within asphaltene clusters and their subsequent slowed motion and diffusion within the cluster. We relate the measured scaling parameters ξ to cluster sizes which we find to be of the order of 2.2-4.4nm for an effective sphere diameter. These sizes are in agreement with the typical values reported in the literature as well as with the small-angle X-ray scattering experiments performed on our samples [1].

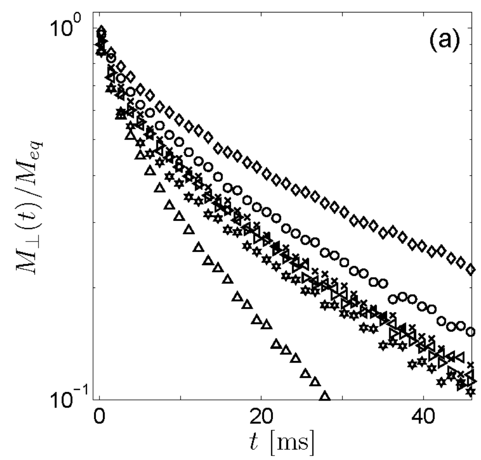

Fig. 1. Normalized transverse relaxation for Oil 2 with varying amounts of asphaltene. The T_2 relaxation is multi-exponential, and the decay rates are faster for samples with higher asphaltene content.

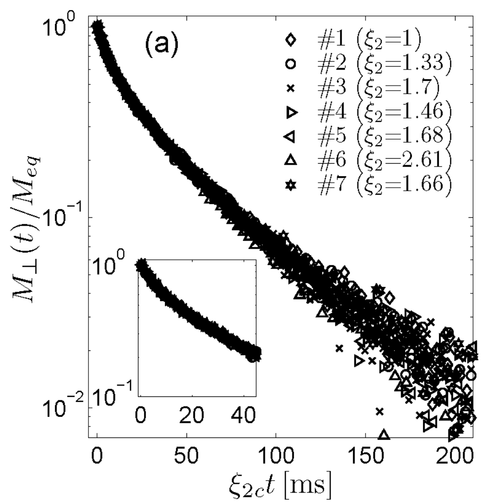

Fig. 1. Same data as shown in Figure 1, with the time axis rescaled by ξ_2.

References

[1] Zielinski, L., Saha, I., Freed, D.E., Hürlimann, M.D., *Langmuir*, Article ASAP,DOI: 10.1021/la904309k