ULTRASONIC VELOCITY CHARACTERISATION OF ASPHALTENE AGGREGATION IN TOLUENE SOLUTIONS

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Introduction

Asphaltenes are the heaviest, most polar and aromatic constituents of petroleum [Sheu and Mullins, 1995] crucial to the formation of highly-stable water-in-crude oil emulsions (WOEs) [Sjoblom et al., 2003]. Asphaltene 'monomers' are highly-polydisperse [Andreatta et al., 2005]; a generic molecular structure comprises a polycyclic aromatic hydrocarbon (PAH) core(s) and aliphatic appendages [Sheu and Mullins, 1995]. Asphaltenes create a rigid 'skin' around water droplets when present in nanoaggregate form, which maintainins stability of the emulsion matrix [Jeribi et al., 2002]. We use high-precision ultrasonic velocity measurements to study asphaltene nanoaggregation in toluene. When measured as a function of asphaltene concentration, sound velocity detects nanoaggregation as an intersection of two linear behaviours (Figure 1) [Zielinski et al. 1986], corresponding to the critical nanoaggregate concentration [Andreatta et al., 2005]. We discover variability around the asphaltene aggregation point which has not yet been studied in detail. This variability is attributed to the polydispersity [Andreatta et al., 2005] of the asphaltene fraction. We propose asphaltenes to aggregate within a critical nanoaggregation region (CNR) which we estimate using statistical constrained optimisation. The coefficient of determination R^2 is used to evaluate the fit of linear models [Zielinski et al., 1986] in monomeric and nanoaggregate concentration regions.

Nanoaggregation of asphaltenes is governed by steric hindrance between alkyl appendages and $\pi - \pi$ attraction between PAH cores [Buenrosto-Gonzalez, 2001]. We treat asphaltenes using ruthenium ion catalysed oxidation (RICO) to obtain structural information about their appendages and alkyl bridges between aromatic units [Peng et al., 1999]. An associative relationship is found between structural RICO information and the CNR properties.

Results

Figure 1 illustrates ultrasonic velocity measurements of four different petroleum asphaltene samples in toluene. In general, asphaltene aggregation behaviour was found to have an association with the degree of steric hindrance and aromatic branching. An increased proportion of alkyl appendages and decreased aromatic branching correlated with a higher variation of speed of sound within the CNR and lower R^2 of the fitted linear regressions. For example, asphaltene E1 (plot (a)) has the lowest proportion of alkyl appendages and the highest R^2 for both regressions with the narrowest CNR. In contrast, E3 (plot (c)) has highest steric hindrance effects and the lowest proportion of aromatic branching, accompanied by the highest variation in ultrasonic velocity around nanoaggregation and the lowest R^2 in both regions. Similar associations are found for the remaining samples. It may be observed that the width of the CNR (red shading) is highly-varied across the four samples. In this study we present combined data from ultrasonic velocimetry, mass spectral measurements and statistical modelling to approach some of the unresolved questions about asphaltene nanoaggregation.
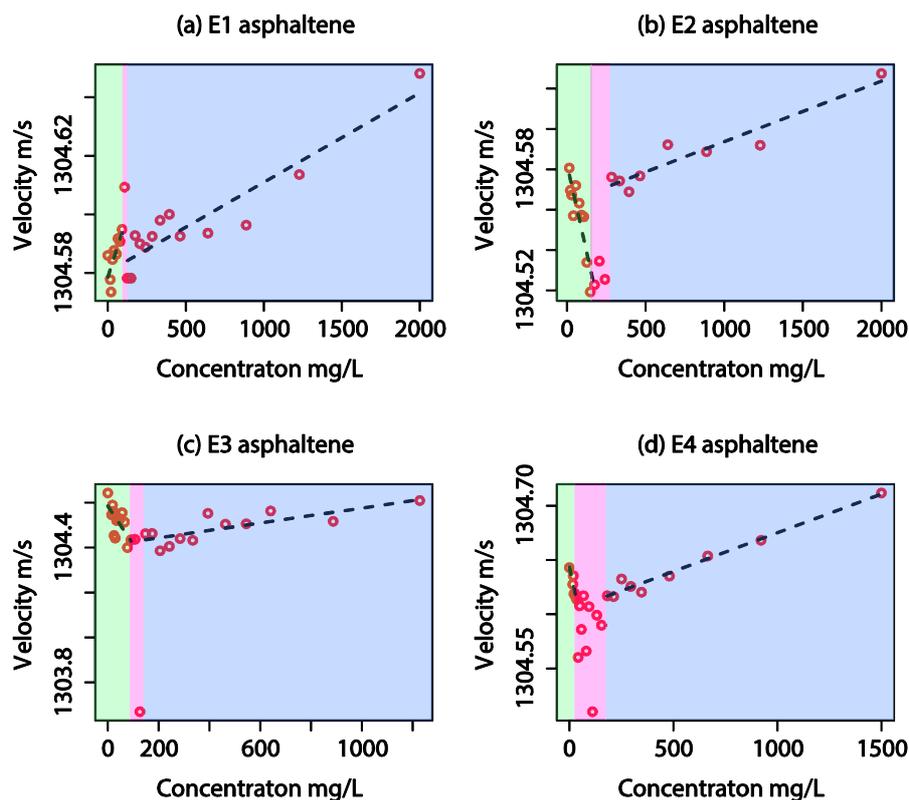
Figure 1 *Ultrasonic velocity measurements of asphaltenes E1, E2, E3 and E4. Green, red and blue shading represent monomer, CNR and aggregated regions respectively. Dashed lines represent the estimated linear models, derivation is given in Zielinski et al., 1986.*

References

Andreatta, G., Bostrom, N., Mullins, O.C., 2005. High-*Q* ultrasonic determination of the critical nanoaggregate concentration of asphaltenes and the critical micelle concentration of standard surfactants. Langmuir 21, 2728-2736.

Buenrostro-Gonzalez, E., Groenzin, H., Lira-Galeana, C., Mullins, O.C., 2001. The overriding chemical principles that define asphaltenes. Energy & Fuels 15, 972-978.

Jeribi, M., Almir-Assad, B., Langevin, D., Henaut, I., Argillier, J.F., 2002. Adsorption kinetics of asphaltenes at liquid interfaces. Journal of Colloid and Interface Science 256, 268-272.

Peng, P., Fu, J., Sheng, G., 1999. Ruthenium-ions-catalyzed oxidation of an immature asphaltene: structural features and biomarker distribution. Energy & Fuels 13, 266-277.

Sheu, E.Y., Mullins, O.C., 1995. Asphaltenes: Fundamentals and Applications. Plenum Press, New York.

Sjoblom, J., Aske, N., Auflem, H., Brandal, O., Harve, T.E., et al., 2003. Our current understanding of water-in-crude oil emulsions. Recent characterization techniques and high pressure performance. Advances in Colloid and Interface Science 100-102, 399–473.

Zielinski, R., Ikeda, S., Nomura, H., Kato, S., 1986. Adiabatic compressibility of Alkyltrimethylammonium bromides in aqueous solutions. Journal of Colloid and Interface Science 119, 398-408.