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STRUCTURE AND FUNCTION OF ASPHALTENES: A GEOCHEMICAL AND ULTRASOUND STUDY

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Asphaltenes are the most important components causing blockages in oil pipelines and fouling in refineries, which lead to enormous costs. They are also responsible for the formation of tar mats in petroleum reservoirs, which can impede crude oil recovery (Wilhelms and Larter, 1994). Despite the amount of effort that has been expended on studying these nanoparticles, there is a great deal of debate surrounding a number of their fundamental properties. For instance does the solution behaviour of associating molecules better explain the aggregation of asphaltene-containing systems, where the high viscosity of bitumen and asphaltenic mixtures is related to their proximity to the glass transition (Sirota, 2005) as compared to the classical colloidal model. In this study, we integrate petroleum geochemistry with ultrasonic spectroscopy to gain new insights into the aggregation properties of asphaltenes.

Our working hypothesis is that the asphaltenes under certain conditions of solvent, ionic strength and type of ion, form vesicles, and that the swelling of the vesicles by solvent increases the volume occupied by asphaltene particles. A glass transition may then occur due to excluded volume effects amongst the particles (see e.g. Tanaka, 2000). We have isolated asphaltenes from a range of both fresh un-degraded and biodegraded North Sea petroleums as well as the associated Kimmeridge source rock bitumen. The asphaltenes are firstly extracted with acetone and then oxidised with a mixture of hydrogen peroxide and acetic acid – this released both adsorbed and occluded molecules including the biomarkers and *n*-alkanes (Liao *et al*., 2006). The biomarkers freed by the above chemical treatment will have been originally trapped within within these vesicles in the body of the asphaltene, without interference from the other moieties that are covalent-bonded to the asphaltene molecular structures. One of the most intriguing results is the control on *n*-alkane length. In fresh oil there is a maximum in the *n*-alkane carbon number distribution at n-C_{17} for the both the maltene and adsorbed fractions whereas the occluded fraction shows a maximum at about n-C_{27}. Heavily biodegraded oil, where there are no *n*-alkanes present in the maltene fraction, show a maximum in the *n*-alkane distribution at about n-C_{28} for both the occluded and adsorbed fractions. A similar type of behaviour is followed by the source rock bitumen in that the *n*-alkane distribution maximises at about n-C_{27}. These differences in asphaltene properties correlate with changes in acoustic attenuation spectra for the same crude oil and bitumen fractions dispersed in toluene as shown below.

When we diluted fresh North Sea oil with 50% toluene, we observed that the oil, when swilled around the walls of the glass container, had a grainy appearance (see inset to Fig. 1). In the acoustic spectroscope sample cell, as the sample levels went up and down it left rivulets of oil streaming down the walls. This indicates phase instability. The attenuation spectrum contained breaks and departures (see ▲ in Fig. 1) from the normal power law dependence. Where the curves depart from power law dependence, this indicates that the samples change DURING a single frequency sweep. The fresh oil therefore shows clear signs of a changing size of the scattering entities. In contrast, the toluene diluted biodegraded oils and Kimmeridge bitumen (including the isolated asphaltenes) behave exactly like the toluene in which they are suspended, indicating that no measurable excess scattering was occurring. These results demonstrate the potential that lies in bringing together the normally disparate disciplines of organic geochemistry and ultrasonic spectroscopy in order to improve our fundamental understanding of the asphaltene fraction of oils.

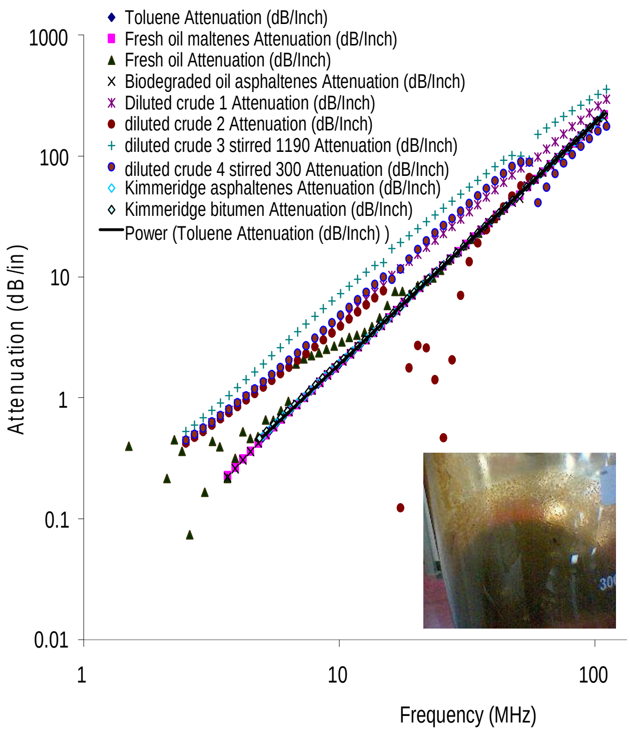

Figure 1. Ultrasound attenuation plotted as a function of frequency for a range of North Sea crude oils, source rock bitumen and isolated asphaltenes.

REFERENCES

Wilhelms, A. and Larter, S.R. (1994) Origin of tar mats in petroleum reservoirs. Part I: Introduction and case studies. *Marine and Petroleum Geology* **11**, 418-441.

Sirota, E.B. (2005) Physical Structure of Asphaltenes. *Energy and Fuels* **19**, 1290 – 1296.

Liao, Z., Geng, A., Graciaa, A., Creux, P., Chrostowska, A. and Zhang, Y. (2006) Saturated hydrocarbons occluded inside asphaltene structures and their geochemical significance, as exemplified by two Venezuelan oils. *Organic Geochemistry* **37**, 291-303.

Tanaka, H. (2000) Viscoelastic phase separation. *Journal of Physics: Condensed Matter* **12**, R207–R264.