Purification of petroporphyrins from bitumen and impact on self assembly of asphaltenes

I. D. Singh, D. Savithri, D. Knepper, and P. K. Kilpatrick

Department of Chemical and Biomolecular Engineering,
University of Notre Dame, Notre Dame, IN 46556
*(*peter.kilpatrick@nd.edu)*

Petroporphyrins play a crucial role not only in the processing and application of bitumen/heavy crudes but also in the production and transportation of heavy oils as well. A comprehensive method (flow diagram, page 10) for isolating, purifying, and characterizing metallo-petroporphyrins (MPPs) from heavy petroleum feedstocks has been developed and applied to an Athabasca bitumen. The method produces MPPs that are at least 20-25% pure based on both metal and UV-visible spectrophotometric analyses, which are the purest yet obtained from petroleum fluids. The challenges in obtaining MPPs of this purity largely relates to their intimate commingling and molecular entanglement with asphaltenes, a challenge that is largely overcome here by dissociating the asphaltenic aggregates in warm o-dichlorobenzene, a solvent known to be outstanding in solvating and dissociating asphaltenes. Our methods not only resulted in MPPs of unprecedented purity, but also in fractional recoveries in our extraction and chromatographic steps approaching 100% The MPPs were characterized by ICP (inductively coupled plasma) metal analysis, elemental analysis, laser desorption MS (mass spectrometry), UV-visible spectrophotometry, and multinuclear nmr. The MPPs in this Athabasca bitumen are predominantly of the vanadyl variety, with V/Ni mass ratios of 2.2 to 2.6. The porphyrin rings in these MPPs are very substantially benzo-substituted, with nearly 50+% of the MPPs possessing these functionalities. This is consistent with a molecular structure that would be expected to be intimately associated with asphaltenic aggregates.

The aggregate forming properties of both the asphaltenes in this Athabasca bitumen, as well as asphaltenes altered by doping with increasing amounts of purified MPPs, were measured by Pulse Field Gradient Spin-Echo Nuclear Magnetic Resonance spectroscopy (PFGSE NMR). This technique measures the diffusion coefficients of proton-active solutes. Solutions were made of asphaltenes free of MPPs, as well as of asphaltenic aggregates which have been doped by adding selectively hundreds and thousands of ppm levels of vanadyl MPPs to the asphaltenes. Remarkably, these modest levels of dopants dramatically increase the diffusion coefficients by a factor of 3, and reduce the aggregate radius by a corresponding factor. Thus, vanadyl MPPs appear to always solvate asphaltenic aggregates and break them up into smaller aggregates. This may not be the case with nickel MPPs, something we tend to explore further. It may also be the case that this result is only true for MPPs which are separable from the asphaltenes, but may not be the case for MPPs that are covalently bound to asphaltenes.