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Self-assembly of Asphaltenes: Enthalpy, Entropy of Depletion and Dynamics at Crossover I-experimental NATALIA LISITZA, DENISE FREED, PABITRA SEN, YI-QIAO SONG, Schlumberger-Doll Research — The continuous rise of global demand for energy and the difficulty of significantly increasing production have driven the petroleum industry to develop much more difficult oil reservoirs, such as deep-water fields. Asphaltenes, naturally-occurring large aromatic molecules in crude oils, are known to be the "cholesterol" of petroleum because they self-associate to form solid aggregates and eventually clog the production pipes and the rocks. An extraordinary amount of work using many analytical techniques has been applied to elucidate the properties of asphaltenes. However, many fundamental issues, such as the molecular architecture and the aggregation mechanisms, are still in debate. Here we use NMR to detect asphaltene aggregation in toluene solutions and to obtain both the enthalpy and entropy of this process. We observe an abrupt drop of the asphaltene diffusion constant which is indicative of a molecular conformation (shape) change. This change is intimately related to or possibly a prerequisite of the aggregation. The entropy of aggregation was found to be positive due to the excluded volume effect for the solvent. This is reminiscent of the depletion entropy force, which is considered to be the driving force for the aggregation of much large artificial nanoparticles.

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