**Asphaltene deposition experiment and modeling in the service of thermodynamics**

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**Highlights**

* Monitoring asphaltenes deposition using a fully immersed Quartz Crystal Resonator
* Experimental identification of deposition mechanism by liquid alkane titrations
* Experimental identification of deposition mechanism by depressurization of gas-dissolved oils
* Deposition modeling and comparison to experimental data

**1. Introduction**

Asphaltenes destabilization and deposition are mainly caused by the expansion of dissolved light alkanes, such as methane, during the petroleum extraction. Based on experimental observations replicating the expansion of light-ends by flowing fixed concentration mixtures of petroleum and liquid alkanes at ambient conditions; deposition models have been developed1,2. In those cases, diffusion-limited equations were computed with measured and realistically fitted input parameters in order to match the experimental observation. Upscaling the diffusive principles of these models to the flow of gas-dissolved oils implies calculations of multiple pressure dependent parameters instead, which increases uncertainties. Additionally, the nature of the precipitant showed a significant effect on the asphaltenes destabilization3. Experimental verifications of the modeled deposition of asphaltenes destabilized by the expansion of light alkanes are very limited in the current literature.

**2. Methods**

Two different apparatus were used to measure the deposited mass of asphaltenes destabilized by addition of liquid n-alkanes:

1. a packed bed of beads apparatus recently developed1 in which an isothermal mixture is continuously flowing at a controlled flow rate.
2. a continuously stirred reactor containing a fully immersed Quartz Crystal Resonator (QCR) indirectly recording asphaltenes deposited mass on its surface during isothermal titrations of liquid n-alkanes.

The QCR is an advantageous technique that requires very few deposit (sensitive to nano grams) and working in pressurized fluids4. Therefore, we also performed isothermal constant mass expansions of gas-dissolved systems while recording the deposition with the QCR. In parallel, a centrifugation method was used to measure the mass concentration of aggregated unstable asphaltenes for multiple mixtures of oil and liquid n-alkanes. The interplaying effects of time and evolution of the composition were studied. Based on experimental investigations, the initial goal was to verify the first principles of the existing models and apply them to the QCR geometry.

**3. Results and discussion**

The comparison of the concentration of unstable asphaltenes (obtained by centrifugation) with the deposition experiments, along with an analysis of the deposition profiles at several conditions enables an identification of the fraction of asphaltenes that can deposit. The possible deposition mechanisms are discussed based on experimental results, i. e. diffusion-limited and reaction-limited. Consequently, this work provides insights for a new model by proposing corrections on the key parameters. Computed deposition rates are then evaluated against the experimental results.

**4. Conclusions**

The validation of a novel deposition model is presented using experimental data recorded from a QCR sensor at ambient pressure and at gas-dissolved conditions. This study provides a major step in the understanding of asphaltenes deposition in industrial conditions, it helps identifying the predominant parameters and the mechanism of their deposition rate. This work does not only provide a validation of the deposition mechanism but mass transport equations combined to high pressure immersed QCR signal interpretation also give us access to a crucial information for the understanding of asphaltenes behavior: the concentration of unstable asphaltenes at all conditions. Thermodynamic models can therefore be challenged against implicitly measured quantities thanks to the findings.

**References**

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