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Analysis of asphaltenes adsorption on surfaces using QCM-D

The adsorption of asphaltenes in crude oil to different surfaces represents an important issue for the petrochemical industry. QCM-D technology can be used to evaluate different approaches to solve such problems. In particular, the ability of QCM-D technology to monitor various structural arrangements of adsorbed materials can be used to understand how asphaltenes adsorb to surfaces.

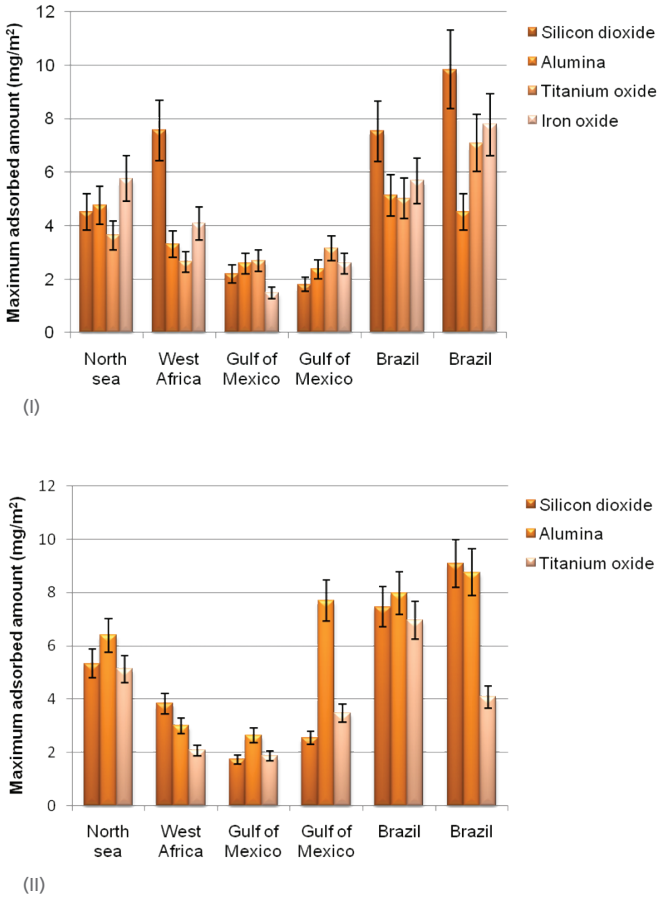
Introduction

Every day, the petroleum industry faces the challenge of handling problems due to fouling, altered wettability and coking. A major cause of these problems is the adsorption of petroleum heavy ends at solid/liquid interfaces that occurs at different stages of oil production. Of the heavy ends in petroleum, asphaltenes are often considered the most problematic because they tend to aggregate and form deposits under certain pressure, temperature and composition conditions.

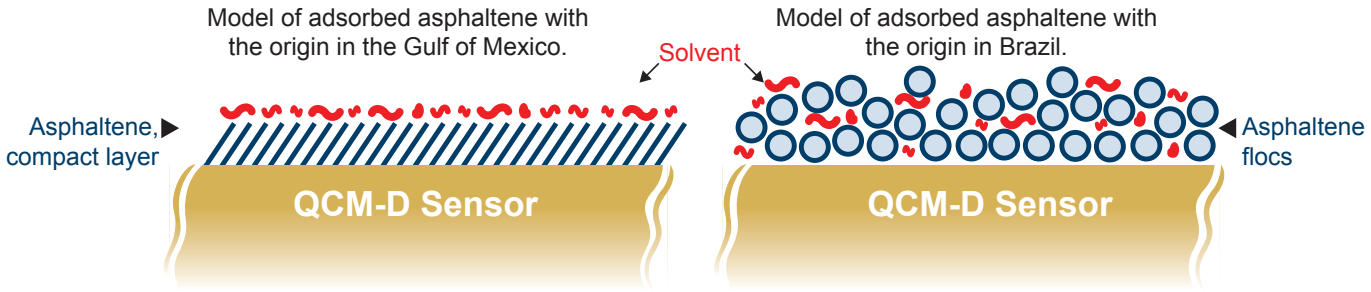
To gain valuable insight into the mechanism of asphaltene deposition, there is a need for fundamental understanding of asphaltene-solid interactions through studying asphaltene adsorption to surfaces. Quartz Crystal Microbalance with Dissipation (QCM-D) monitoring is an acoustic, non-labeling, surface-sensitive technique that provides real-time information on the mass and structure of thin films. This application note describes a recent example of how QCM-D can be used to investigate asphaltene1 surface interactions through characterizing adsorption behavior to surfaces of different materials and under different solvent conditions.

Experimental

This study deals with asphaltenes separated from crude oil. Measurements were taken in different solvents, where the degree of asphaltene stability is high (toluene) or poor (n-alkanes and heptane/toluene mixtures). Differences in the amounts adsorbed and the viscoelastic properties of the adsorbed films were recorded.



[Figure 1]: Amount of asphaltenes adsorbed onto sensors from (I) heptane/toluene (1:1) or (II) toluene. Note that samples were collected from two different sites in Brazil and the Gulf of Mexico, respectively. Redrawn with permission from the authors[1].



[Figure 2]: Illustration of how asphaltenes can adsorb to the surface. Asphaltenes attached to the surface as a compact layer (left) and asphaltenes in the flocculated state (right). Redrawn with permission from the authors[1].

Results and discussion

The adsorption of purified asphaltenes in heptane/toluene and toluene onto four different hydrophilic surfaces (SiO_2, alumina (Al_2O_3), TiO_x and FeO_x) was found to depend mainly on the origin of the crude oils as well as on the solvent conditions.

The maximum amounts adsorbed onto the different surfaces are shown in Figure 1. Note that samples with asphaltenes from oils from the same region of the world behaved similarly; in general, samples from Brazil displayed high adsorption to all surfaces, whereas samples from the Gulf of Mexico displayed low adsorption to all surfaces. It was also noted that most of the asphaltenes had the lowest adsorption to the TiO_x surface.

In addition, the adsorbed layers of asphaltenes of different origins resulted in different dissipation shifts (not shown). This shift indicates that the adsorbed materials vary structurally. For example, asphaltene from Brazil yielded significantly higher dissipation shifts than asphaltene from the Gulf of Mexico, which could be explained by differences in solubilization states. Asphaltene from Brazil was beyond the flocculation point; the authors suggested the structural model shown in Figure 2.

Conclusions

QCM-D enables real-time characterization of asphaltene adsorption onto different surfaces. The adsorbed amounts and characteristics of adsorption depend on the solubility state of the asphaltene as well as its origin. Furthermore, surface adsorption varies to a small extent between different hydrophilic sensor coatings.

Acknowledgements

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References:

[1] Dudasova, D, Silset, A, and Sjöblom, J. Quartz Crystal Microbalance Monitoring of Asphaltene Adsorption/Deposition, Journal of Dispersion Science and Technology 29, 139-146 (2008).

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