A Quartz Crystal Microbalance Study of Adsorption of Asphaltenes and Resins onto Hydrophilic Surfaces

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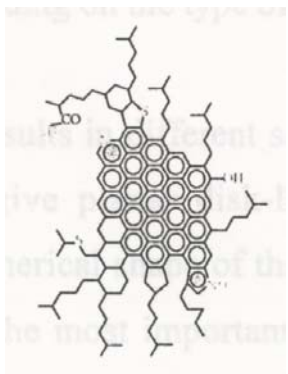
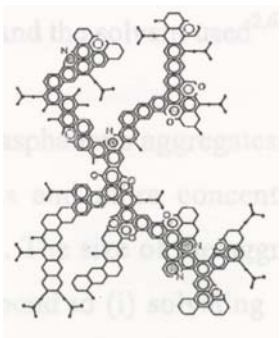
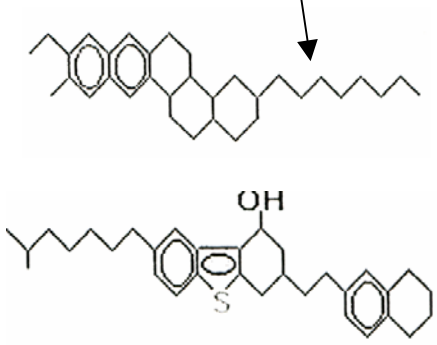
Background

- Asphaltene adsorption and precipitation is of concern during the oil production chain (plugging)
- The adsorption process is difficult to follow by standard optical measuring techniques due to the non-transparent nature of the oil
- We will show that a non-optical technique, the QCM-D allows the adsorption process to be followed

Asphaltenes and resins



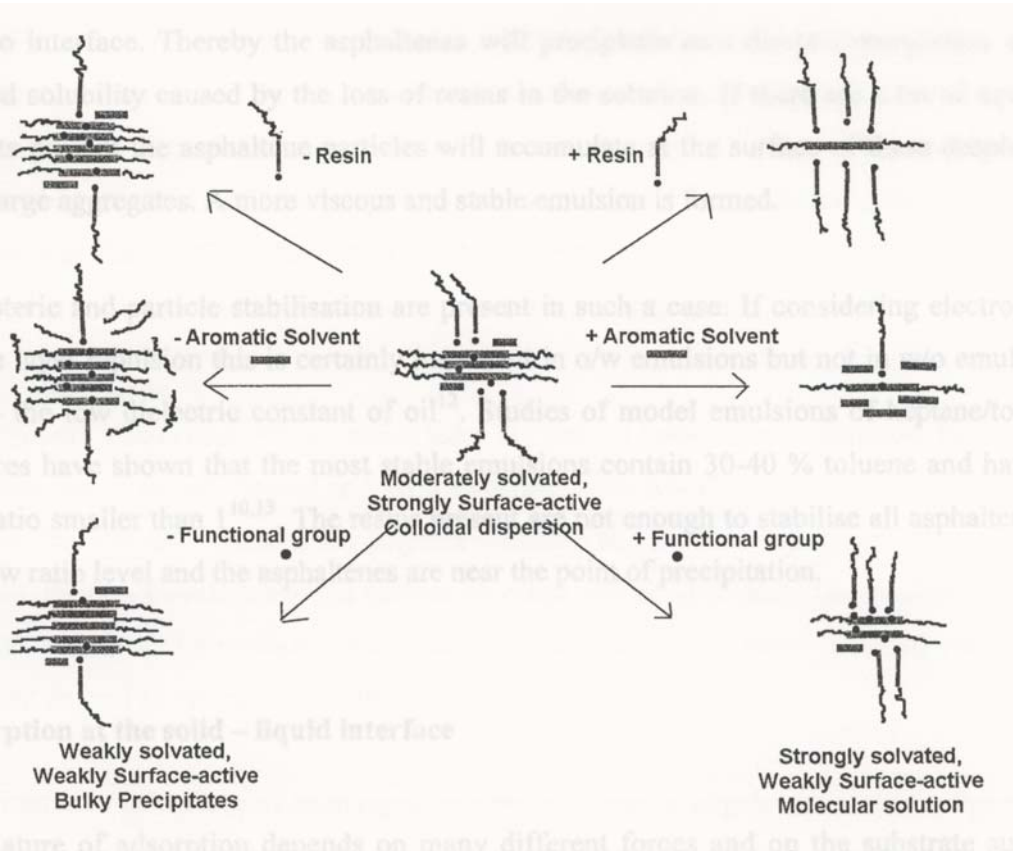




Asphaltenes and resins are solubility classes with heterogeneous chemical structure.

From Dr. G.A. Mansoori, University of Illinois, Chicago

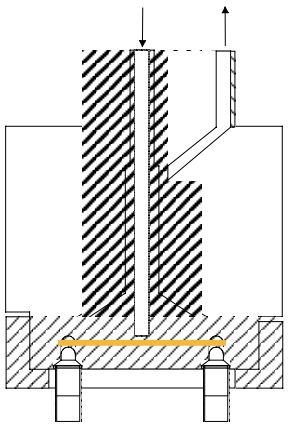
Resins and solvency influence the aggregation of asphaltenes

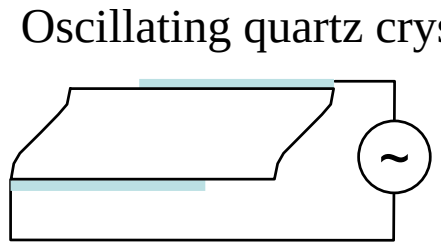


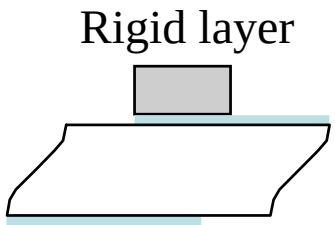
From Mclean & Kilpatrick
JCIS 196, 23 (1997)

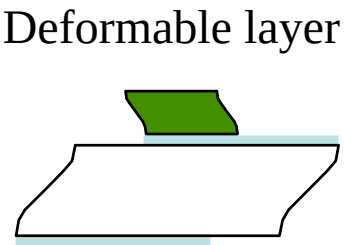
The solubility decreases and the aggregation increases in less aromatic solvent mixtures

QCM-D : Measuring principle







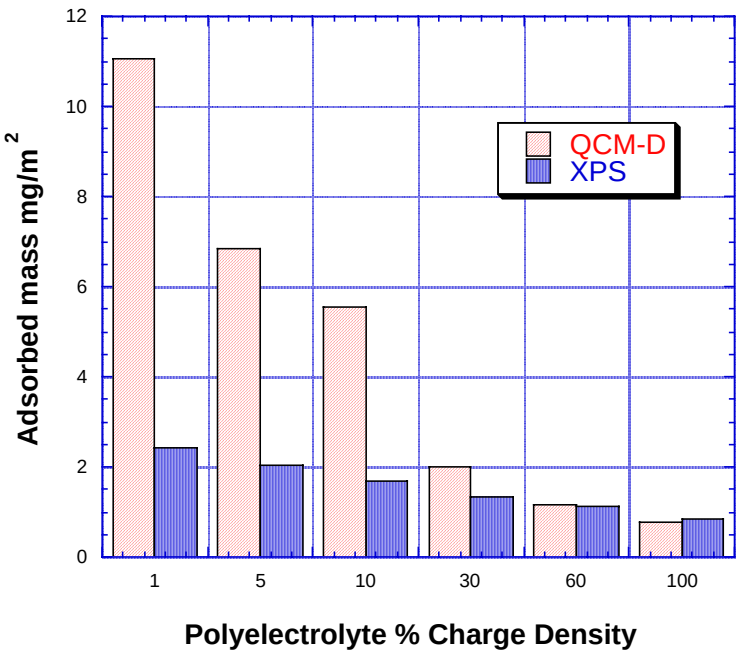


Adsorption leads to:

• changes in resonant frequency, ?f = C?m, related to mass changes, ?m

• changes in the damping of the oscillations, ?D, related to change in the coupling between the crystal and the environment

Sensed mass (QCM) vs. adsorbed mass



The mass sensed with the QCM is often larger than the adsorbed mass.

-hydrodynamically coupled solvent

The solvent effect becomes more important as the dissipation increases

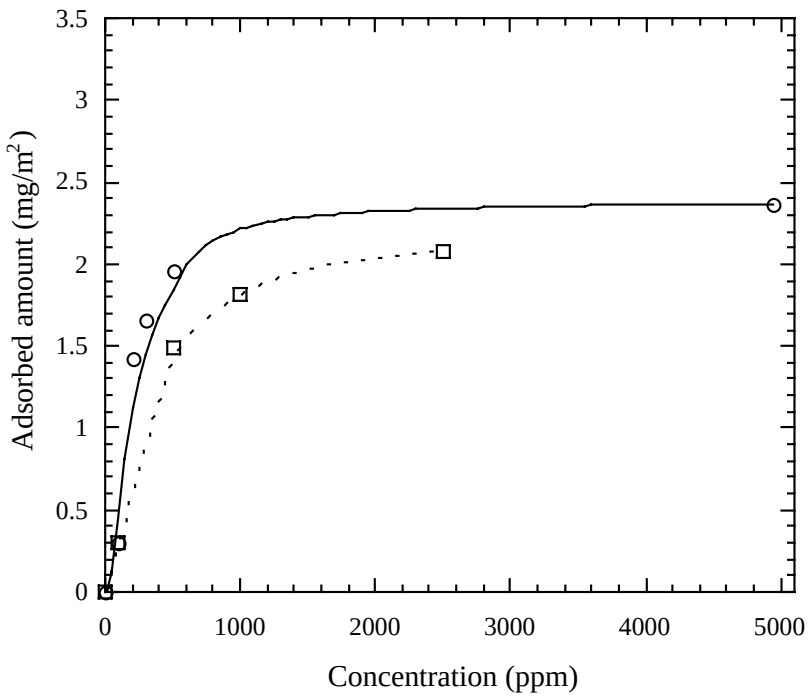
Dissipation change, ?D, and layer structure

Energy dissipation:

Coupling between crystal and environment

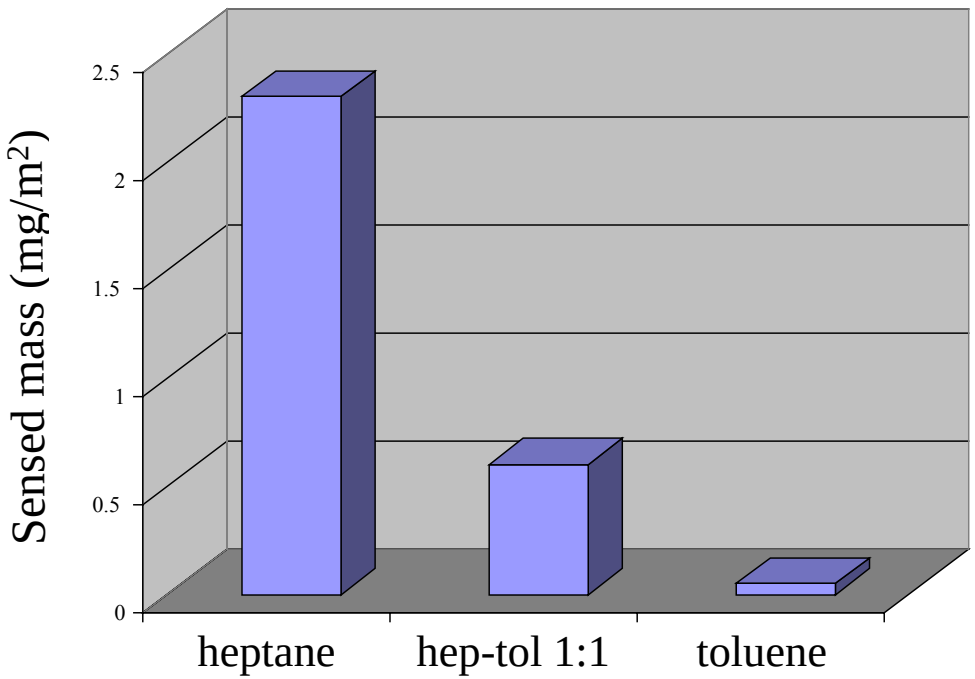
- Property of the environment
- Property of the adsorbed layer
    - thickness
    - segment density distribution
    - surface affinity

Adsorption of resins from heptane



- Rapid adsorption (¡ 10 min.)
- Adsorption plateau 2.3 mg/m^2
  - monolayer
- Low dissipation change
  - rigidly attached layer
- Small desorption on rinsing (< 20%)
  - high surface affinity

Adsorption of resins, effect of solvent quality

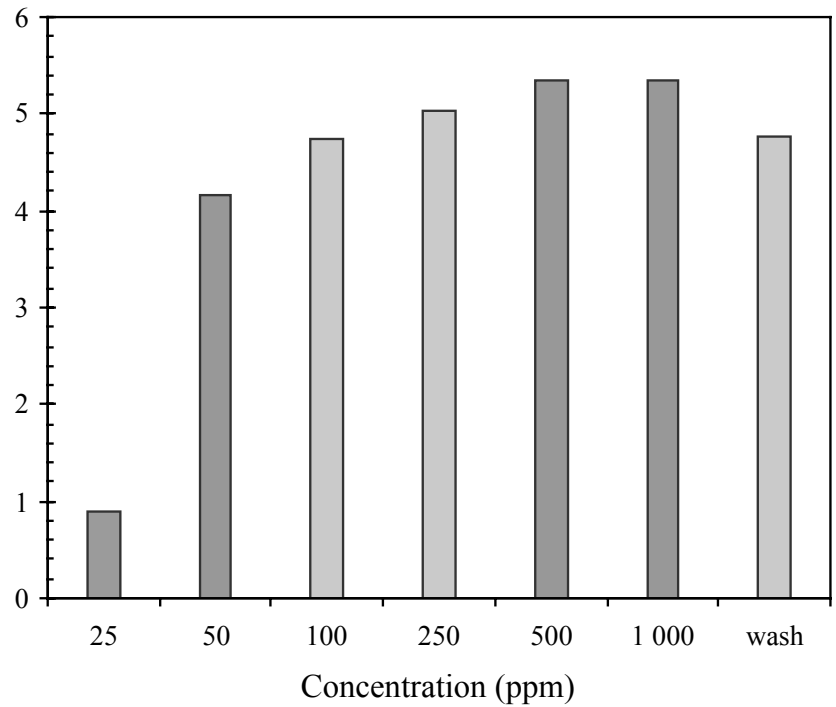


Adsorption decreases when the amount of toluene increases
- due to better solvent quality

Adsorption of asphaltenes from heptane

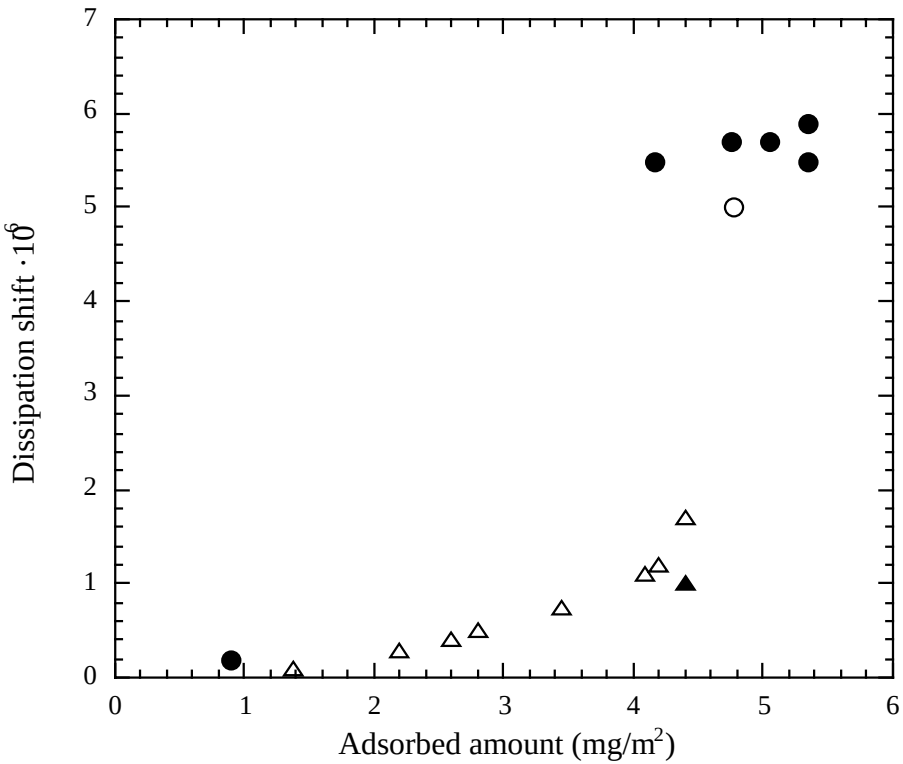
- Precipitation occurs
- No quantitative measurements possible
- Deposited mass is huge!

Adsorption of asphaltenes from heptane-toluene 1:1



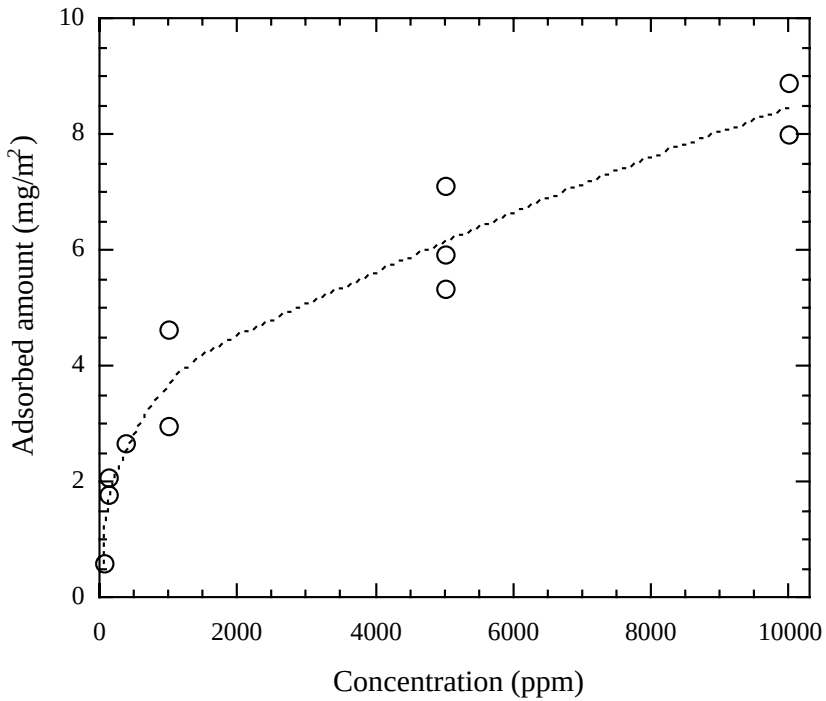
- Adsorption plateau at 5.3 mg/m^2
  - more than typical monolayer
  - aggregate adsorption ?
- Small desorption on rinsing
  - high surface affinity
- Rapid adsorption equilibrium (¡ 10 min)
  - no deposition

Adsorption of asphaltenes from heptane-toluene 1:1
Information obtained from dissipation values



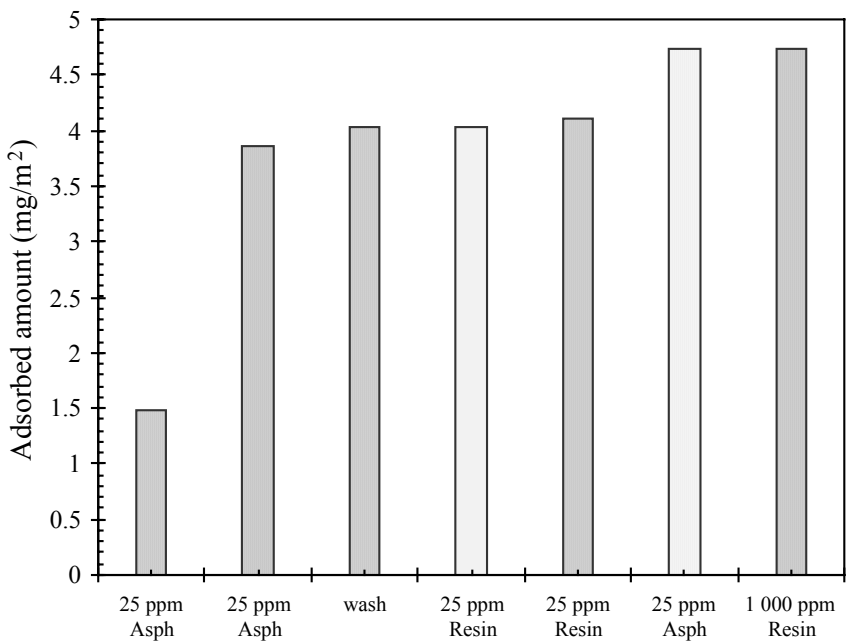
- Small dissipation when sensed mass is less than 4 mg/m^2
  - rigid layer
- High dissipation at higher adsorbed amounts
  - formation of outer layer

Adsorption of asphaltenes from toluene



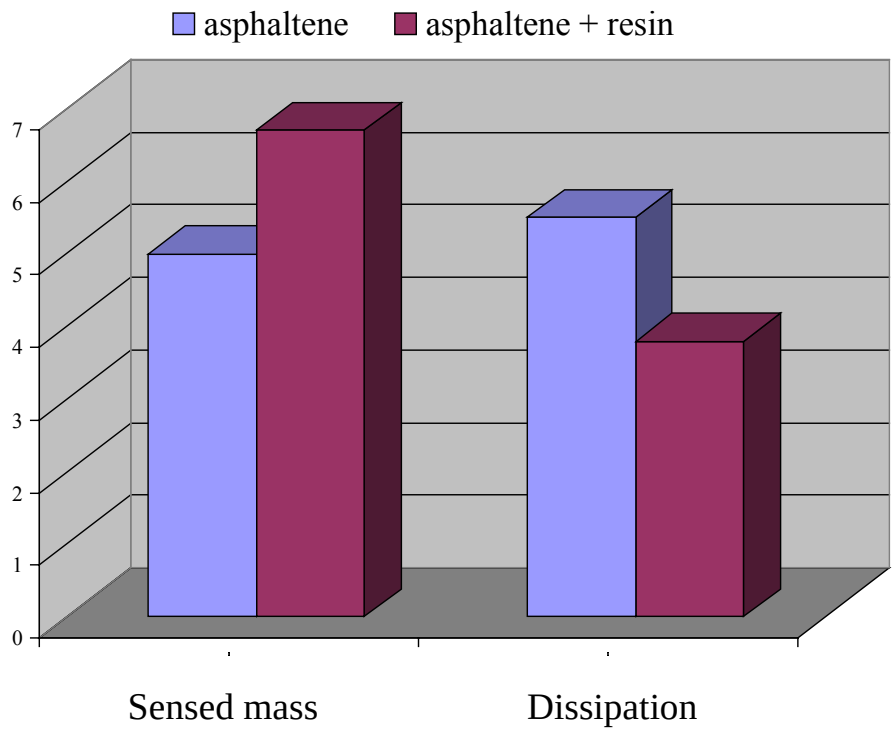
- No real adsorption plateau
- Rapid adsorption (< 10 min.)
- Higher sensed mass than in1:1 heptane-toluene
  - more trapped solvent
- Higher dissipation than in 1:1 heptane-toluene
  - less compact aggregates consistent with better solvent quality

Competitive adsorption of asphaltenes and resins from heptane-toluene 1:1



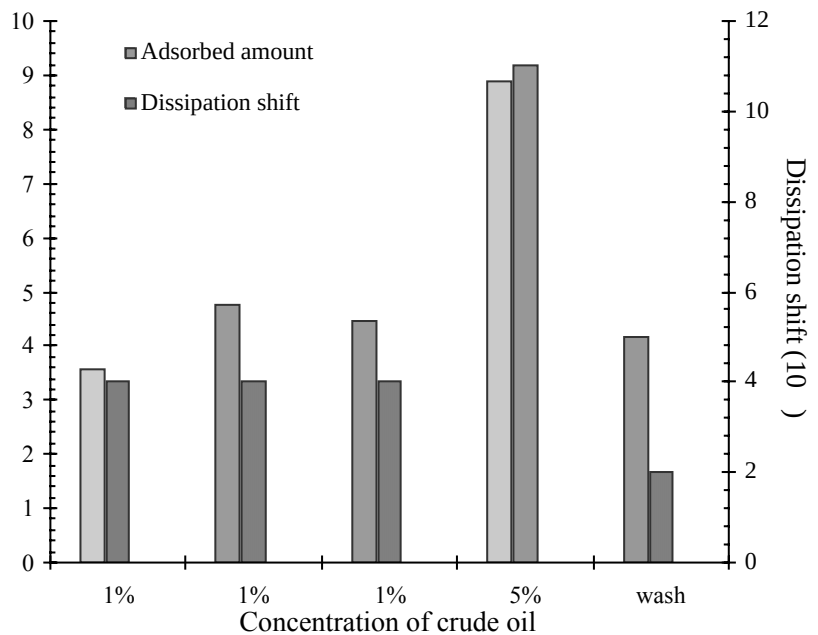
- No adsorption of resins on preadsorbed asphaltenes
  - weak affinity
- No desorption of asphaltenes due to addition of resins.
  - asphaltenes have higher surface affinity

Co-adsorption of asphaltenes (290 ppm) and resins (1380 ppm) from heptane-toluene 1:1



- Higher sensed mass than for pure asphaltene!
  - Presence of resins do not prevent asphaltene adsorption
- Lower dissipation than for pure asphaltene
  - More compact layer

Adsorption from crude oil diluted with a 1:1 toluene - heptane mixture



1%

- Similar sensed mass as for asphaltenes
- Lower dissipation than for asphaltenes

5%

- Larger adsorption and dissipation than in the model systems

Rinsed

- Similar sensed mass to a remaining asphaltene layer.
- Lower dissipation

Conclusions

- Resins adsorb in monolayers
  - Lower adsorption in better solvents
- Asphaltenes adsorb in aggregate form
  - The structure of the layer is sensitive to solvent quality
- Resins cannot displace preadsorbed asphaltenes
- Aggregates adsorb from asphaltene - resin mixtures
- Adsorption from crude oil show many similarities to that from asphaltene-resin model solutions
  - However, weakly attached outer layer prominent at high concentrations