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# The state of asphaltenes in the region we called CMC!?

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# Overview

The region is around 1-10 g /l in toluene!

- Critical Micelle Concentration and why not!
- Data indicating a change
- If not a micelle then what!
- Conclusions

# Asphaltenes

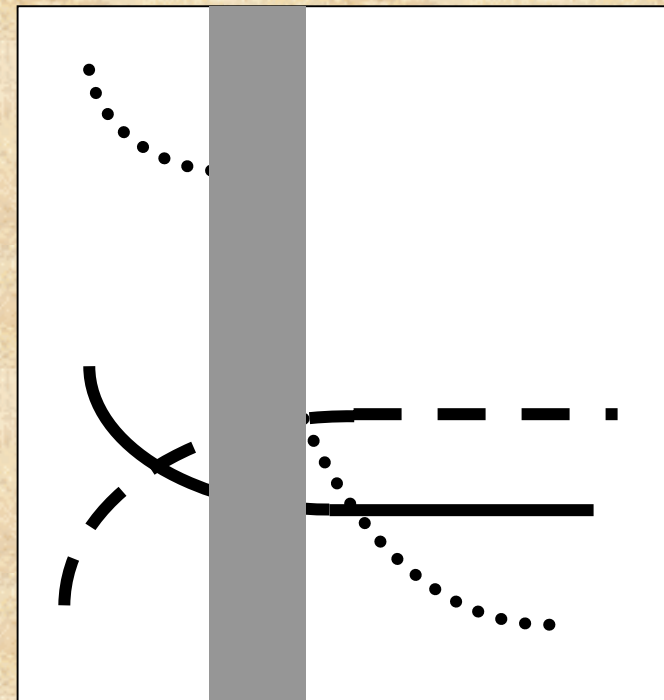
- Complex fraction defined by solubility
- Problematic fractions in industry are only a fraction of the analytical material
- Average structures may not at all represent the real picture
- Aggregation has led to the idea of the critical micelle concentration (CMC) of asphaltenes in solution....

# Facts

- Asphaltenes in solution will dissociate upon dissolution
- No substantial understanding of the actual molecular assembly in crude oil!

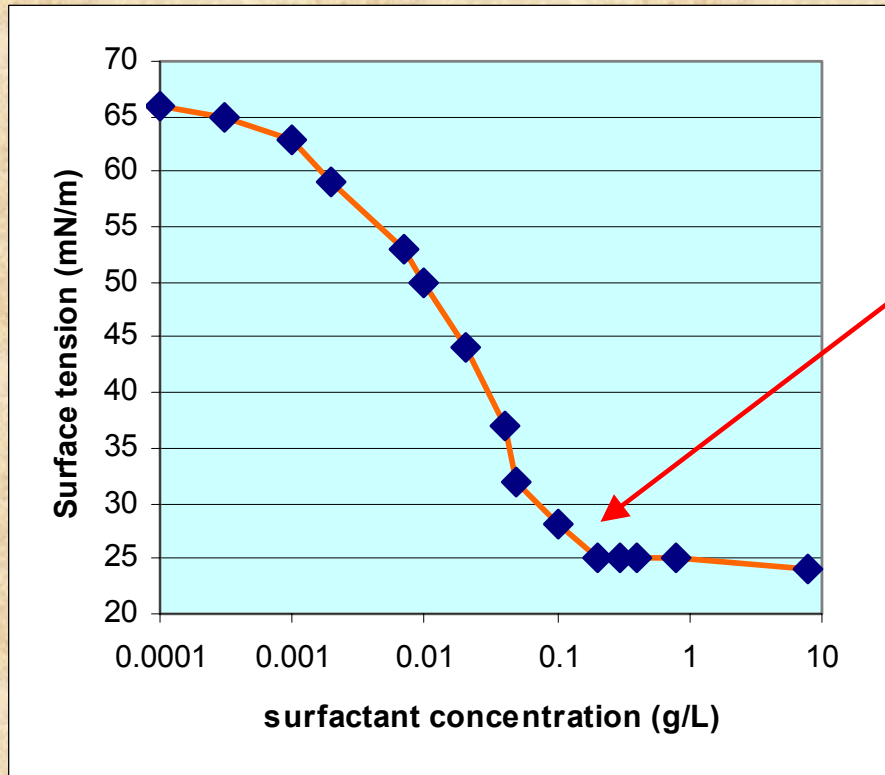
# Critical Micelle Concentration

- Pronounced discontinuity in physical properties of transparent solutions!
- Aggregates being formed
- Nonionic systems higher number of molecules in aggregate
- CMC lower for non-ionic surfactants due to lack of electrical repulsion
- Hydrophobic effect!



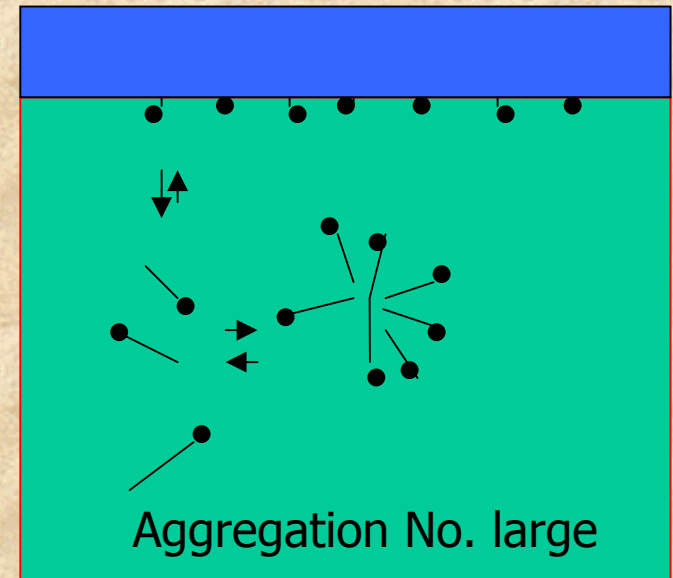
concentration

# CMC determination of surfactant in aqueous solution (dobanol 91-5) Ethoxylated nonionic.



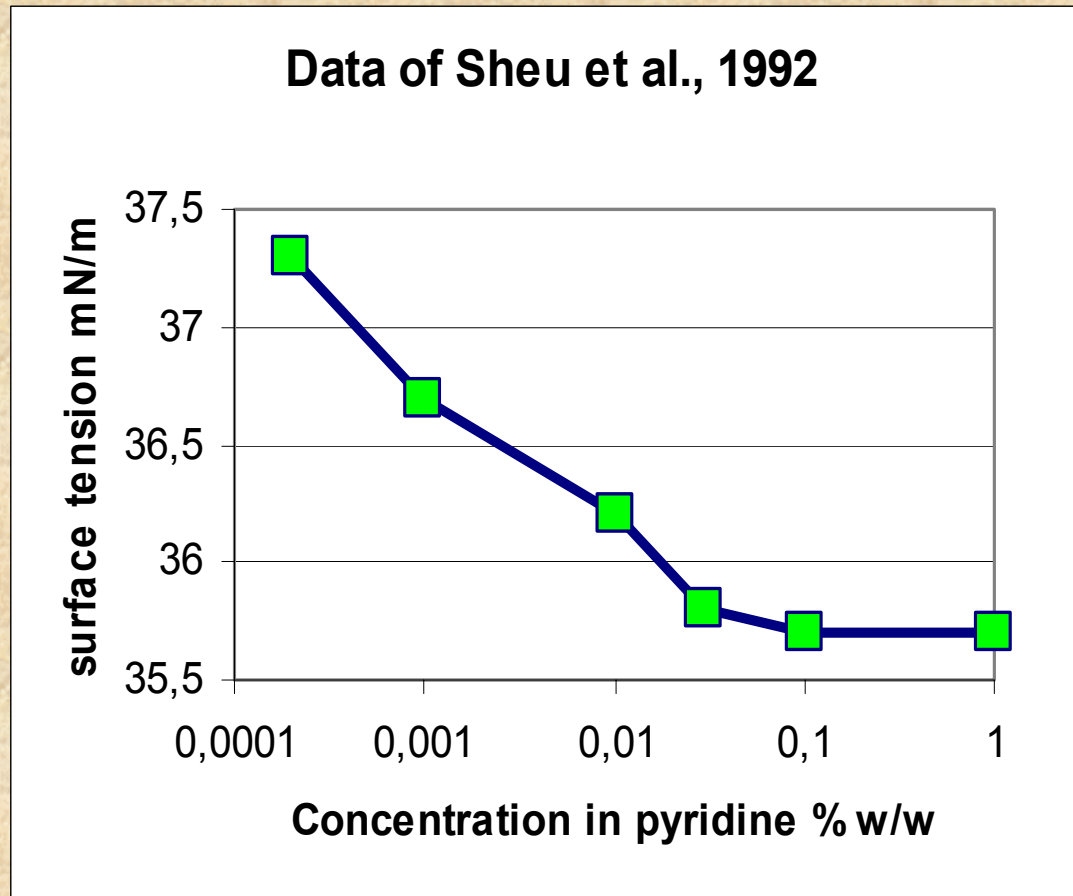
- Plot acc. Gibbs excess equation

CMC



Hydrophobic effect!

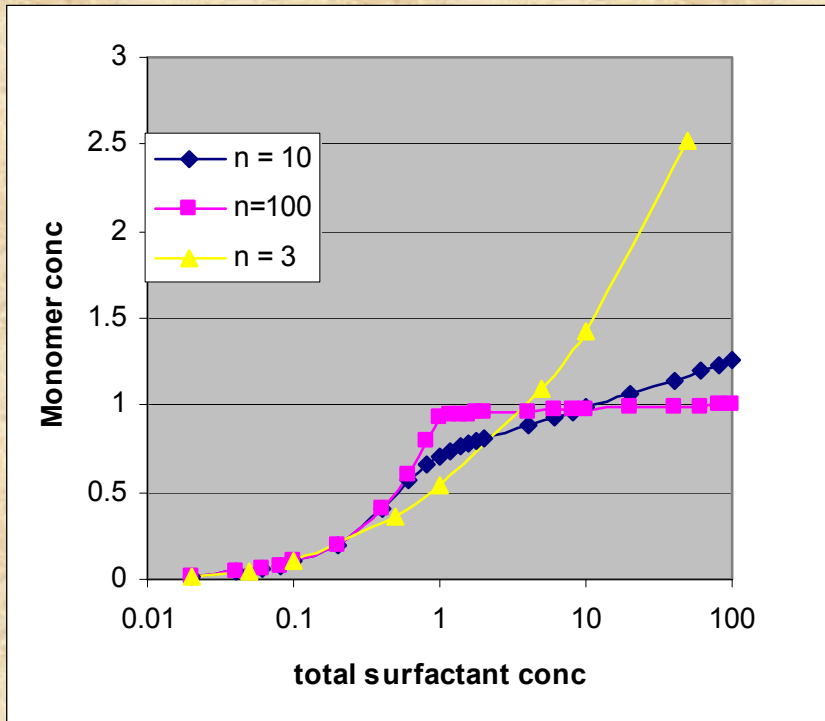
# Surface tension effect of asphaltenes



# Surface tension

- Surface tension was the first technique used in assessing a possible CMC of asphaltenes in solution.
- But analogy is made with aqueous solution:  
In "our" system there is no hydrophobic effect and hence any micellisation will be driven differently.

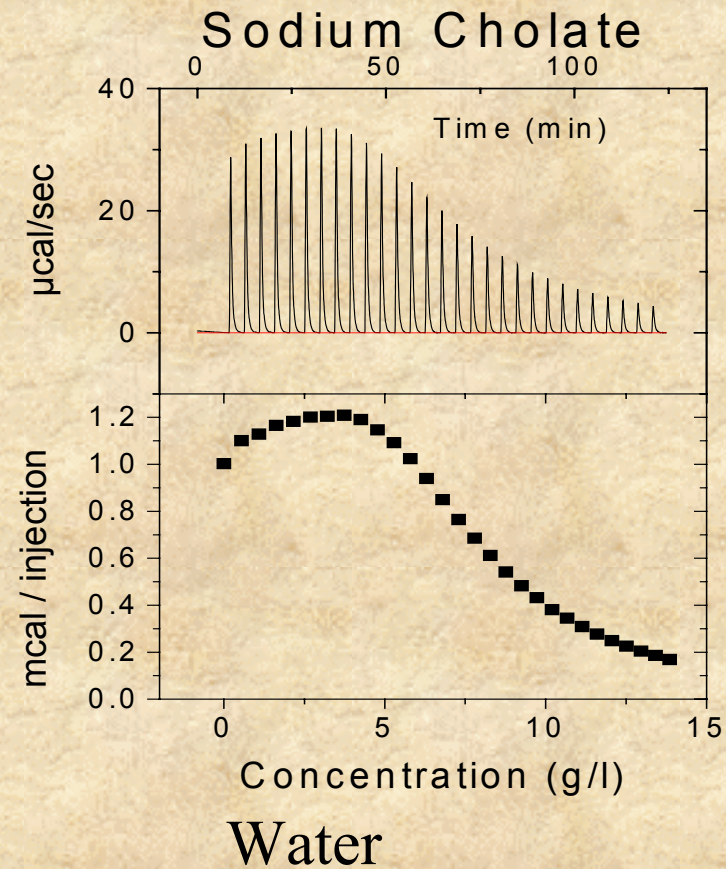
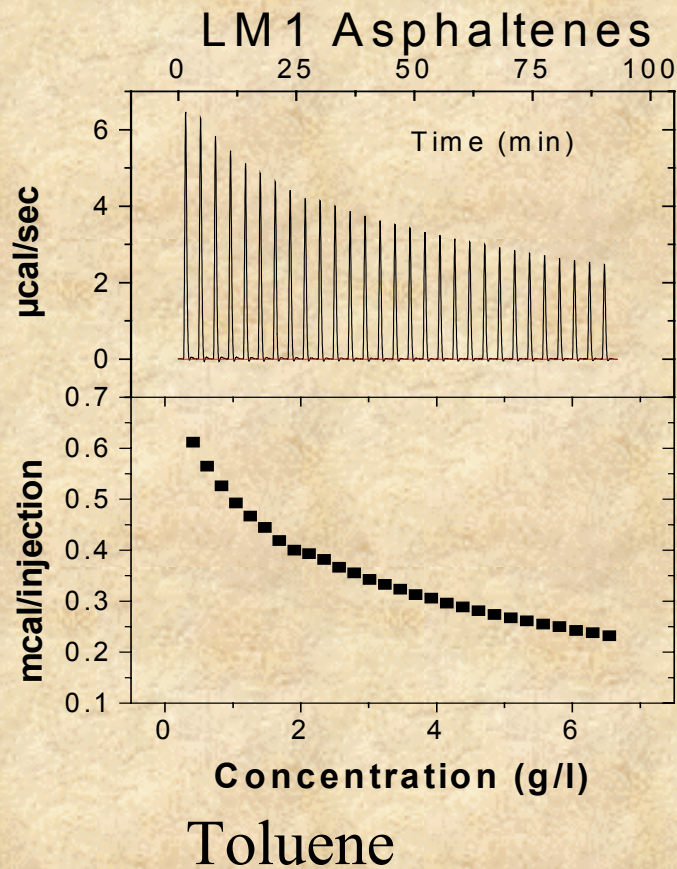
# Surfactant equilibrium as a function of aggregation number



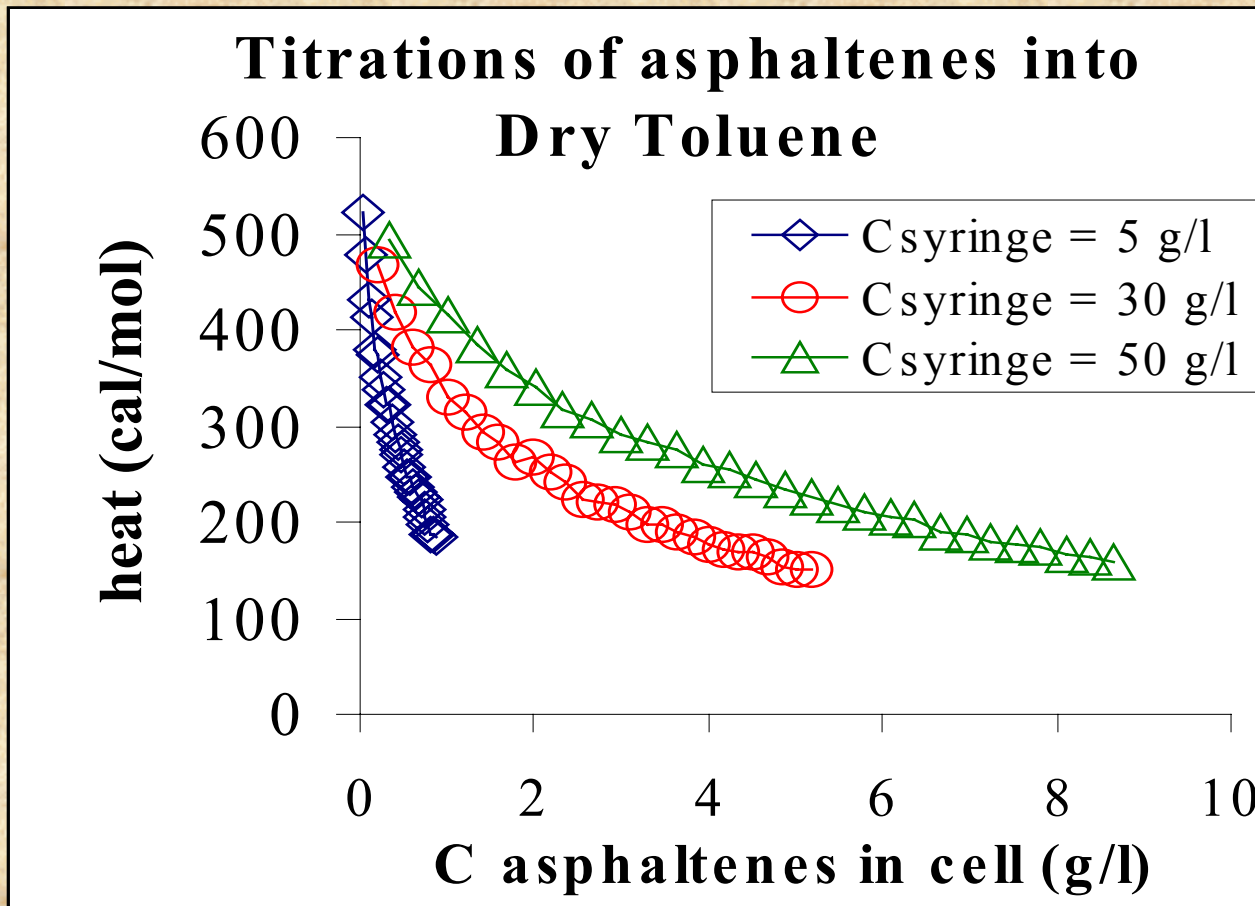
- $[S] = [M] + nK[M]^n$
- N aggreg. No.
- K equilibrium constant
- $[S] = [M]$ ,  $[M] < 1$  and n large
- No CMC for low aggregation numbers

**Therefore technique poor for reversed micelles and not often used...!**

# Heat of dilution using Isothermal Titration Calorimetry

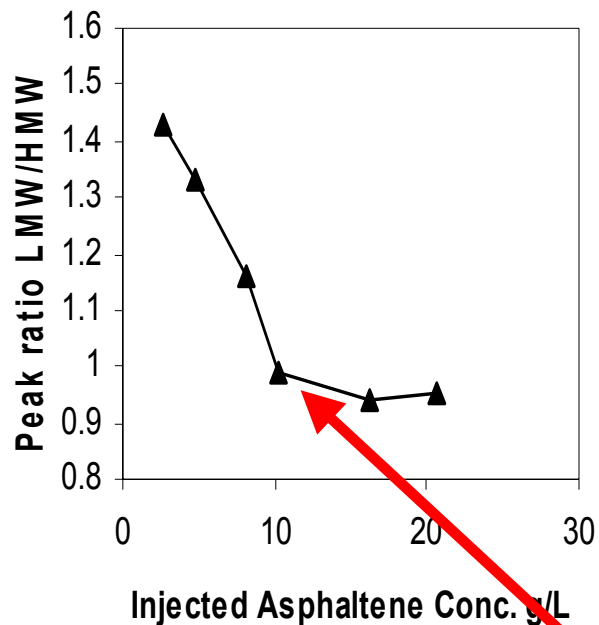


# ITC affected by initial concentration



# HPLC-size exclusion chromatography

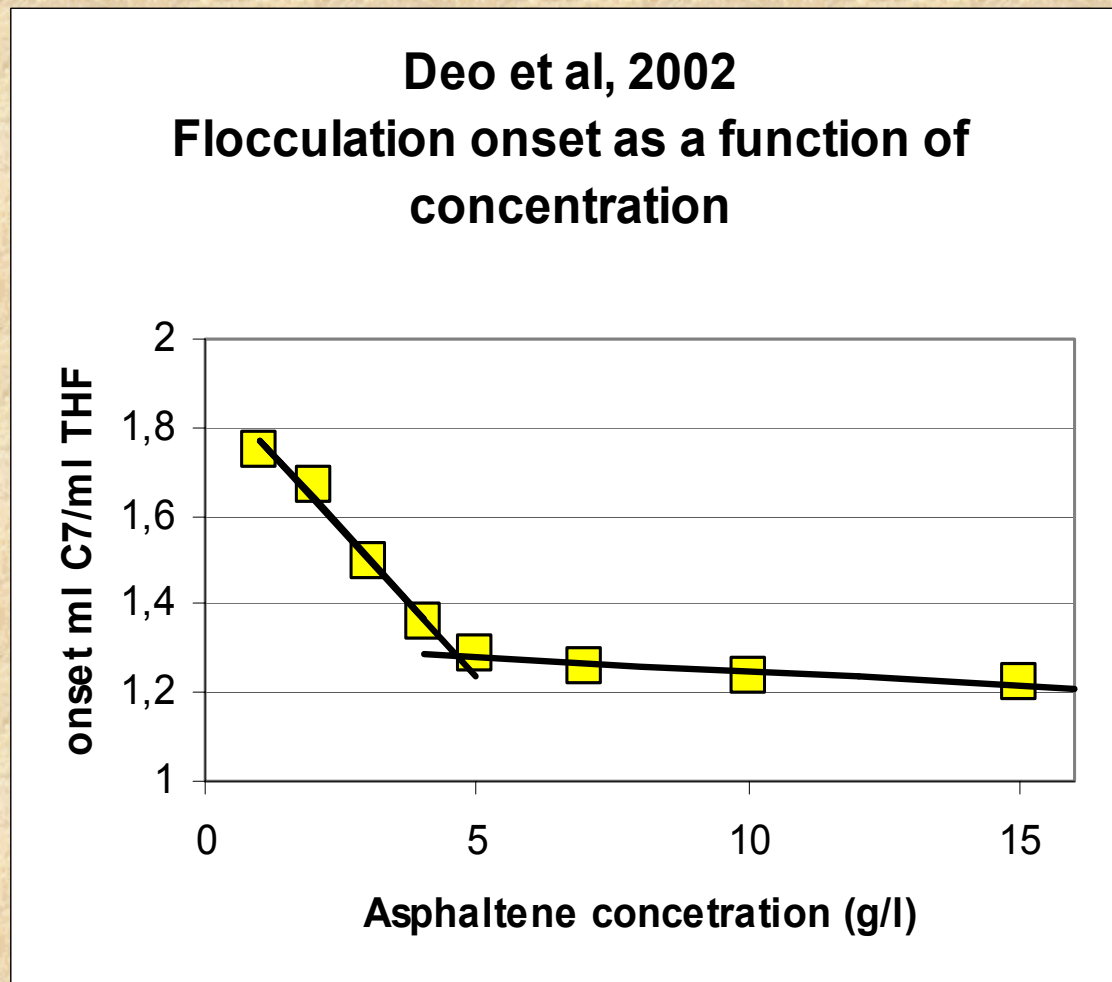
Stepwise increase



- Association reach a steady equilibrium condition after stepwise size increase
- Hence break is NOT a sign of critical micelle concentration

Low MW/High MW constant

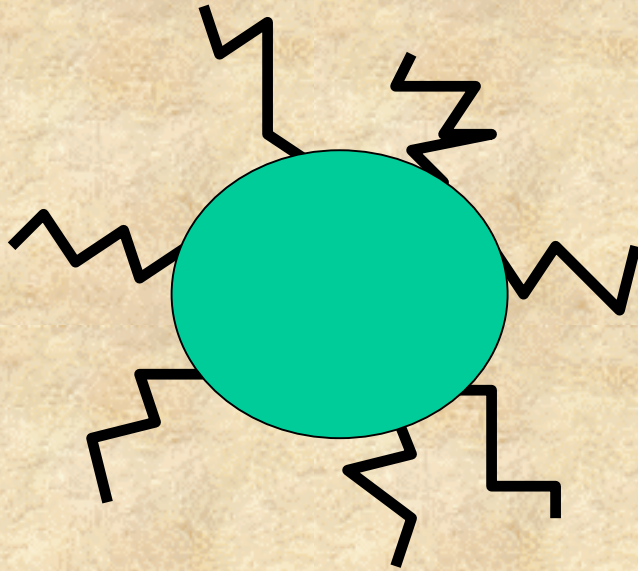
# Flocculation onset of asphaltenes



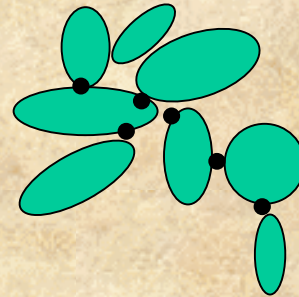
# Alternative mechanism

- Limiting growth effect (SEC; ITC; flocculation onset).
- How: Steric stabilisation by alkyl chains on the outside as well as limited association sites turning "inwards"
- Agreement with the morphology of asphaltenes seen by i.e. AFM (small spheres)
  - Infinite aggregation = gelation

Could be...



or



# Conclusions

- The discontinuity of property-concentration curves for asphaltene solution cannot be related to CMC as
  - There is growth below "CMC": hence no monomer-micelle equilibrium
  - The number of micelles do not increase relative to monomers beyond the discontinuity.
  - One have difficulties to detect these discontinuities even for simple surfactants in non-aqueous media due to low aggregation number

# Conclusions cont.

- Stepwise growth limited aggregation, probably due to formation of steric stabilized micro-aggregates.

Other facts:

solutions are time dependent indicating very slow kinetics in particle formation and reorganization