11th International Conference on Petroleum
Phase Behavior and Fouling June 13-17,2010

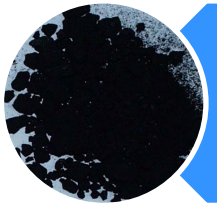
Effect of inhibitors on asphaltene aggregation

Estrella Rogel
ERGC@chevron.com
Chevron Energy Technology Company, Richmond, CA 94801

Content

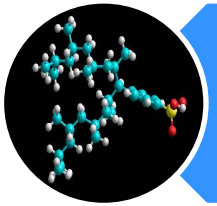
- ✓General uses of asphaltene additives
- ✓Chemical structure
- ✓How do additives work? Classical view
- ✓Molecular thermodynamic modeling
- ✓Results
- ✓Conclusions

Asphaltene Inhibitors



Asphaltene Precipitation or Fouling Inhibitors

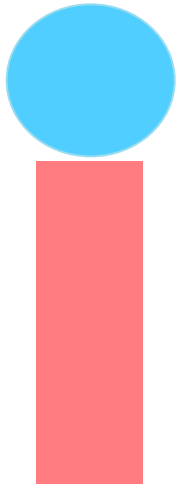
Viscosity Reducers



Reactivity Enhancers

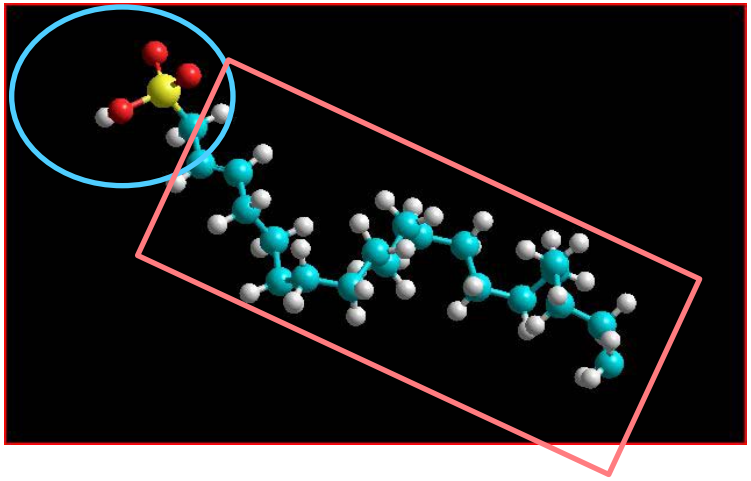
Characteristics of asphaltene additives

- Surfactant-like molecules



Polar Head

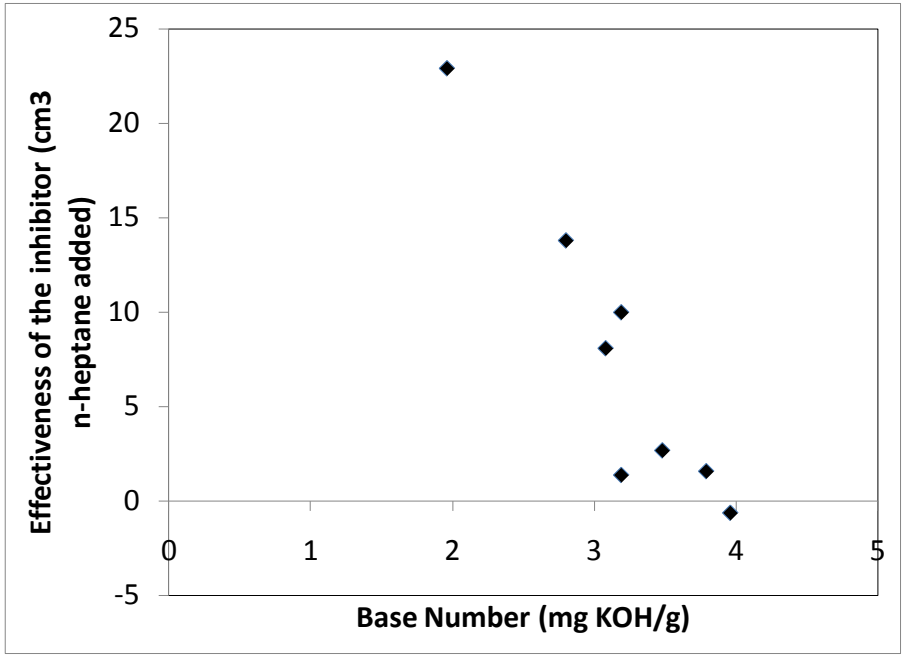
Non polar Tail



Sulfonic acids, Alkyl phenols, Alkyl phenol ethoxylates, Amides, Esters of carboxylic acids, Succinimides, Salicylic Acids and several polymers like Alkyl phenolic resins and Polyvinyl pyrrolidones

Efficiency of inhibitors as related to molecular characteristics. Key aspects

- ✓Polarity of the head group
- ✓Length of the tail
- ✓Acid-base attraction between asphaltenes and amphiphiles
- ✓Solvent Effects

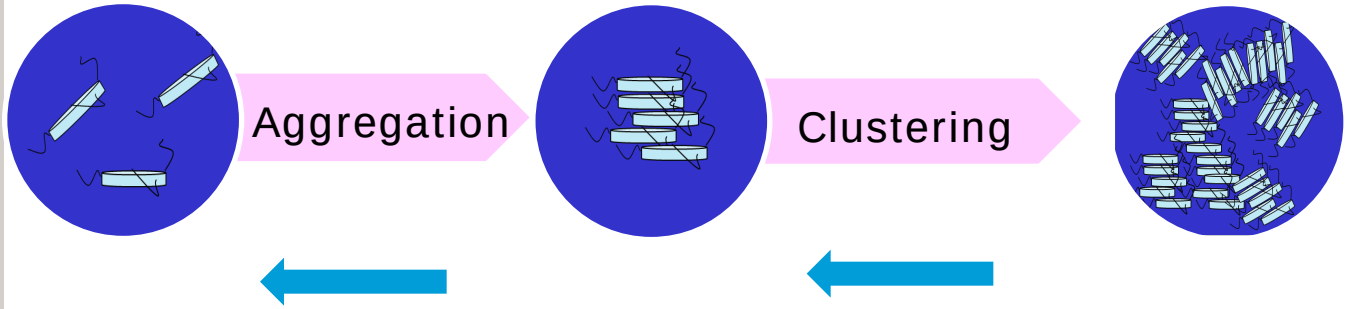


Effect of Dodecyl Benzene Sulfonic Acid on the Flocculation Onset of Different Crude Oils

*Rogel, E. et al. SPE 53998

How do asphaltene inhibitors work?

1. Breaking interactions between asphaltenes
2. Preventing interactions between asphaltene aggregates by forming a steric stabilization layer around them.

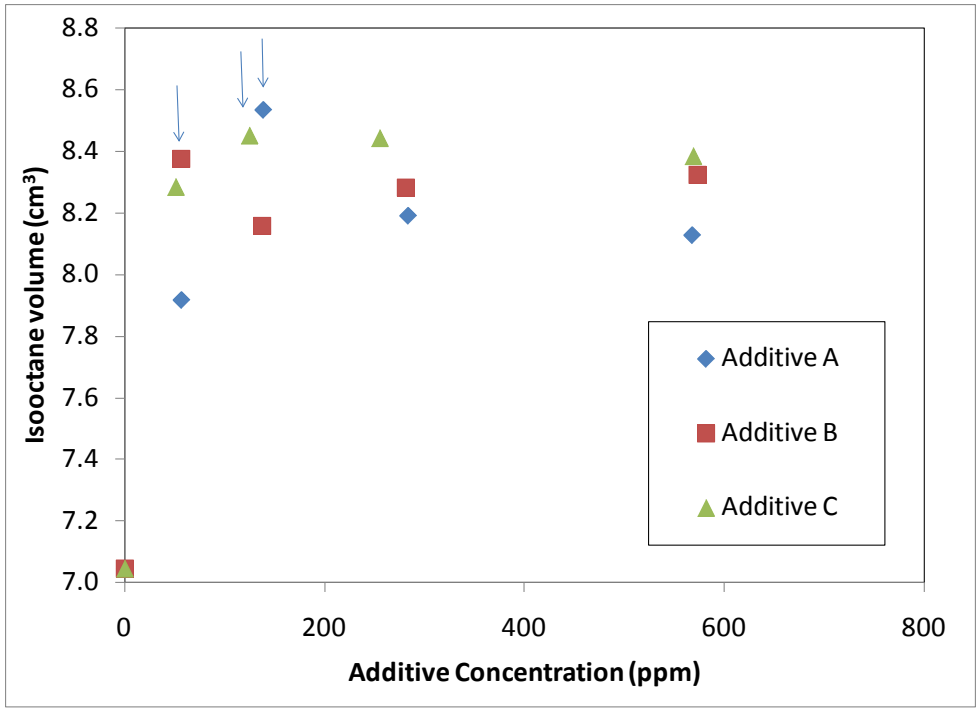


- Asphaltene Nature
- Solvent Power
- Pressure, Temperature

PRECIPITATION

How do asphaltene inhibitors work?

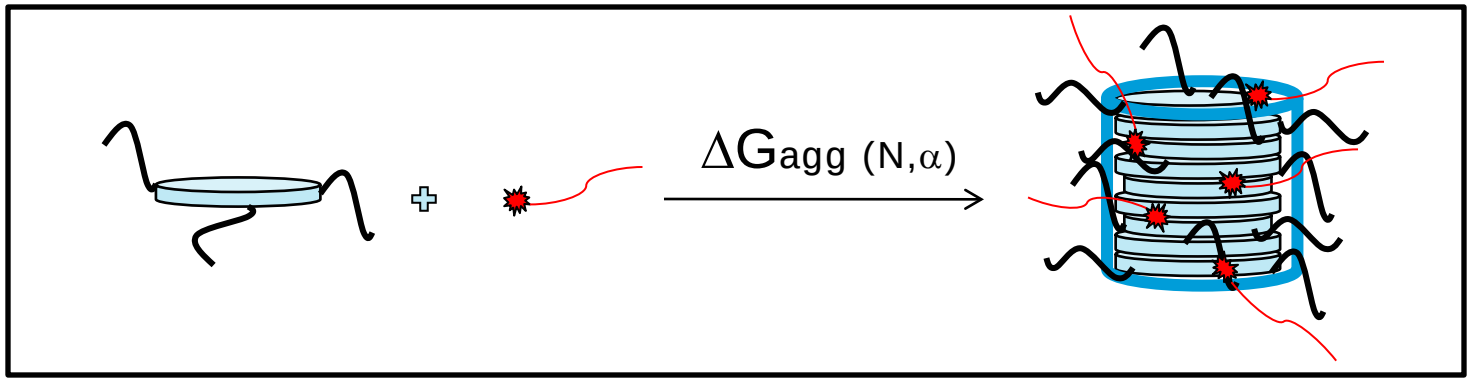
- ✓ Increasing inhibitor concentration decreases its efficiency:
  - ✓ Flocculation Onset
  - ✓ Aggregate Size



Evaluation of additives using flocculation onset titration at low additive/asphaltene ratios (< 1 %)

Molecular Thermodynamic Model

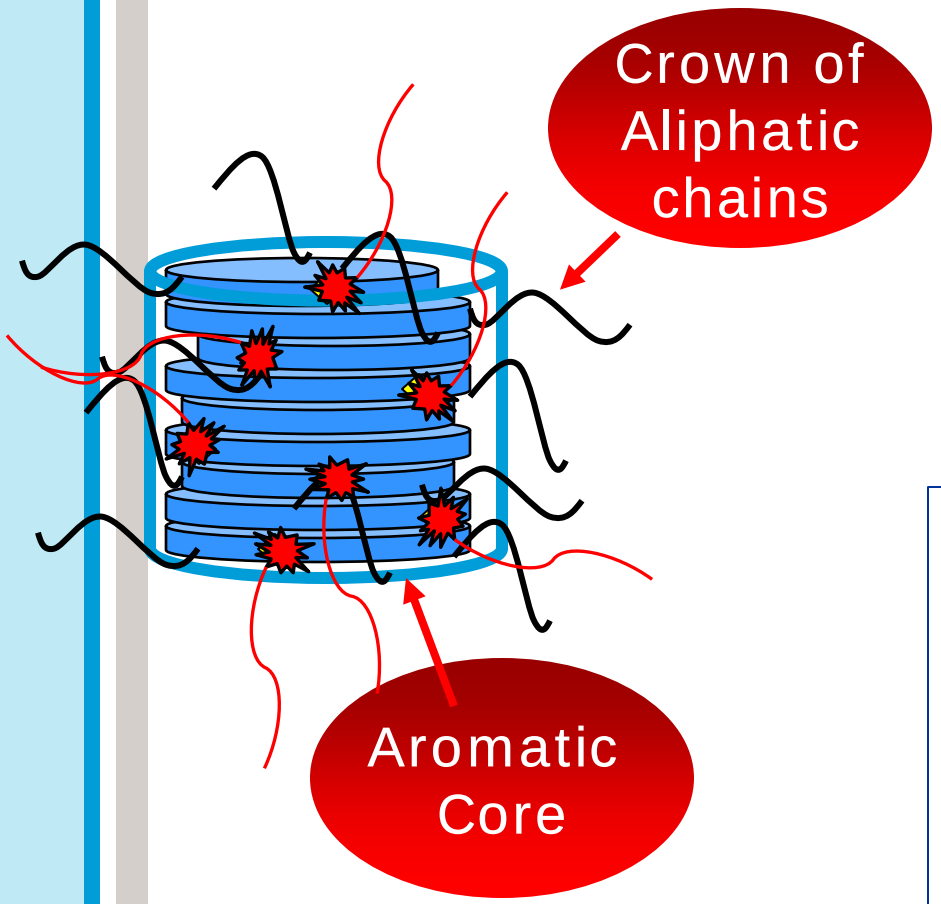
GOAL: to describe the effect of amphiphiles on asphaltene aggregation behavior using a molecular thermodynamic model.



Aggregate size depends on:

Additive solubility in the solvent
Strength of asphaltene-additive interactions
Molecular size of the additive
Molecular characteristics of asphaltenes

Molecular Thermodynamic Model

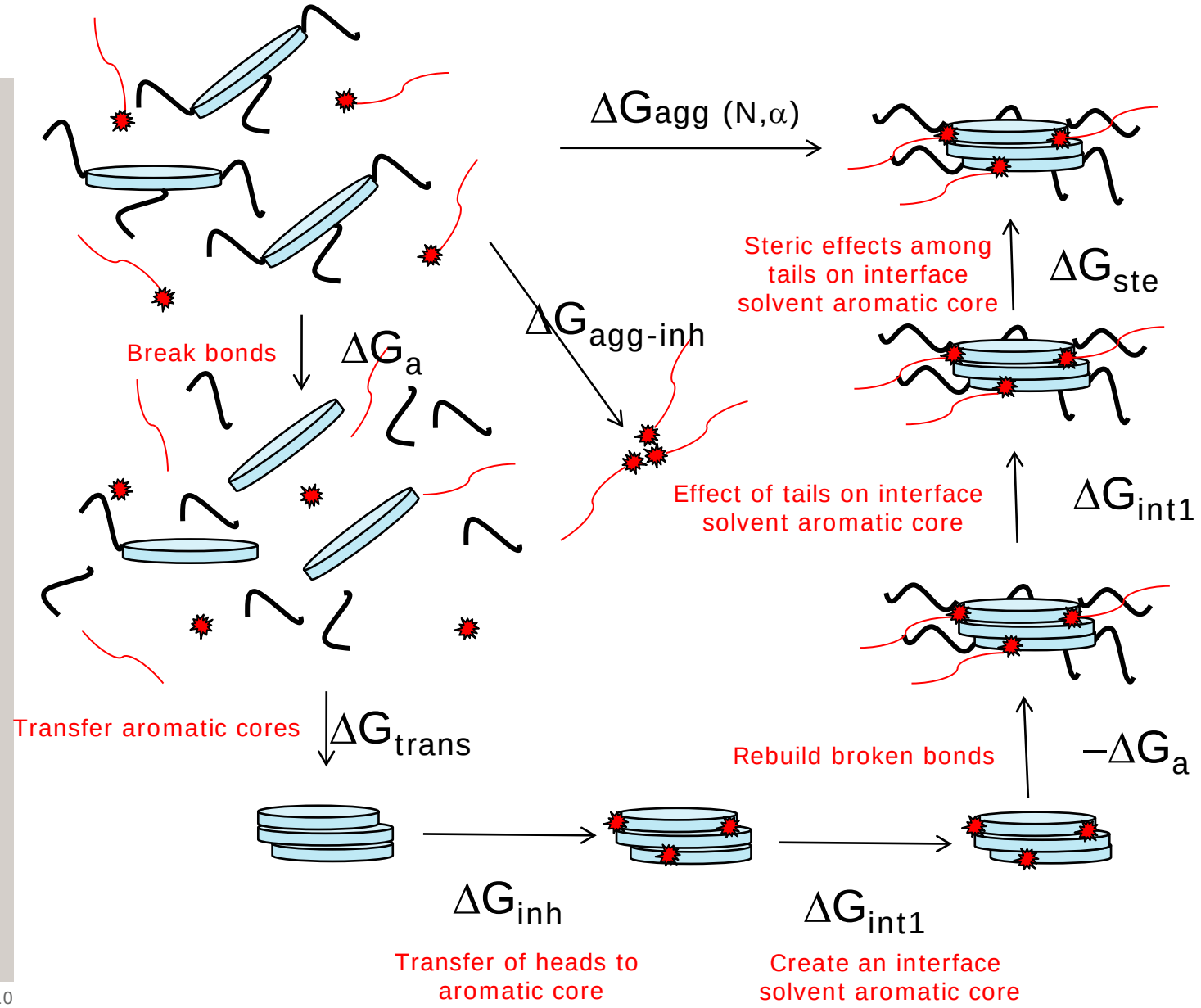


- ✓ Main driving force for aggregation is the attraction between aromatic cores.
- ✓ Aggregation is opposed by interfacial and steric interactions.

- ✓ This model has been successfully used to describe:
  - ✓ Asphaltene aggregation behavior (“c.m.c “or “c.n.a.c”, size distributions)
  - ✓ Effect of resins on asphaltene aggregation.

Rogel, E., *Langmuir* 2002, 2004

Free energy aggregation contributions



Free energy aggregation contributions

$$\Delta G_{agg} = \Delta G_{trans} + \Delta G_{int} + \Delta G_{inh} + \Delta G_{ste}$$

Asphaltenes

$$\Delta G_{trans}/kT = -\alpha \ln X$$

$$X = \exp[-(\Delta H_m/RT)(1-T/T_m) - 1 + (V_l/V_s) - \ln(V_l/V_s) - (V_l/RT)(\delta_s - \delta_l)^2]$$

$$\Delta G_{inh} = (1-\alpha)\, \Delta G_{site\text{-}inhibitor}$$

$$\Delta G_{int} = (1/N)\sigma_A\, (a-a_o)$$

$$\Delta G_{ste}/kT = -(1/N)\ln(1-a_o/a)$$

$$\Delta G_{agg\ inh} = \Delta G_{trans\ inh} + \Delta G_{int\ inh} + \Delta G_{ste\ inh}$$

Inhibitor

$$\Delta G_{trans\ inh}/kT = \ln X_{inh}$$

$$\Delta G_{int\ inh} = \sigma_{mic}\, (A - a_{tail})$$

$$\Delta G_{ste}/kT = -\ln(1-a_{tail}/A)$$

Aggregate Size Distributions. Computational Approach

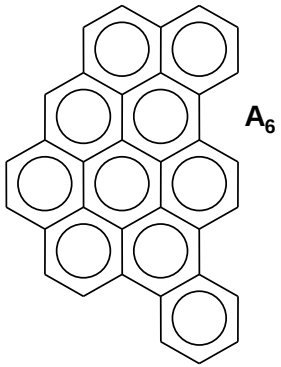
Asphaltenes $X_{N,\alpha} = X_{A1}^{\alpha N} X_{I1}^{(1-\alpha)N} \exp(N\Delta G_{agg}(N, \alpha))$

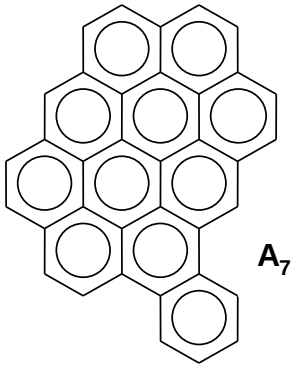
Inhibitor $Y_n = X_{I1}^{n} \exp(n\Delta G_{agg\ inh}(n))$

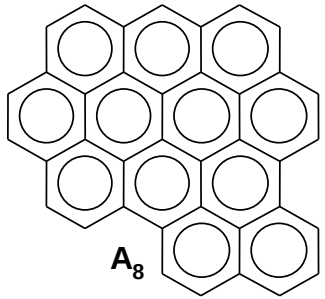
Average Aggregation Numbers

$Nn = \Sigma\ NX_{N,\alpha} / \Sigma\ X_{N,\alpha}$

$Nw = \Sigma N^2 X_{N,\alpha} / \Sigma\ NX_{N,\alpha}$



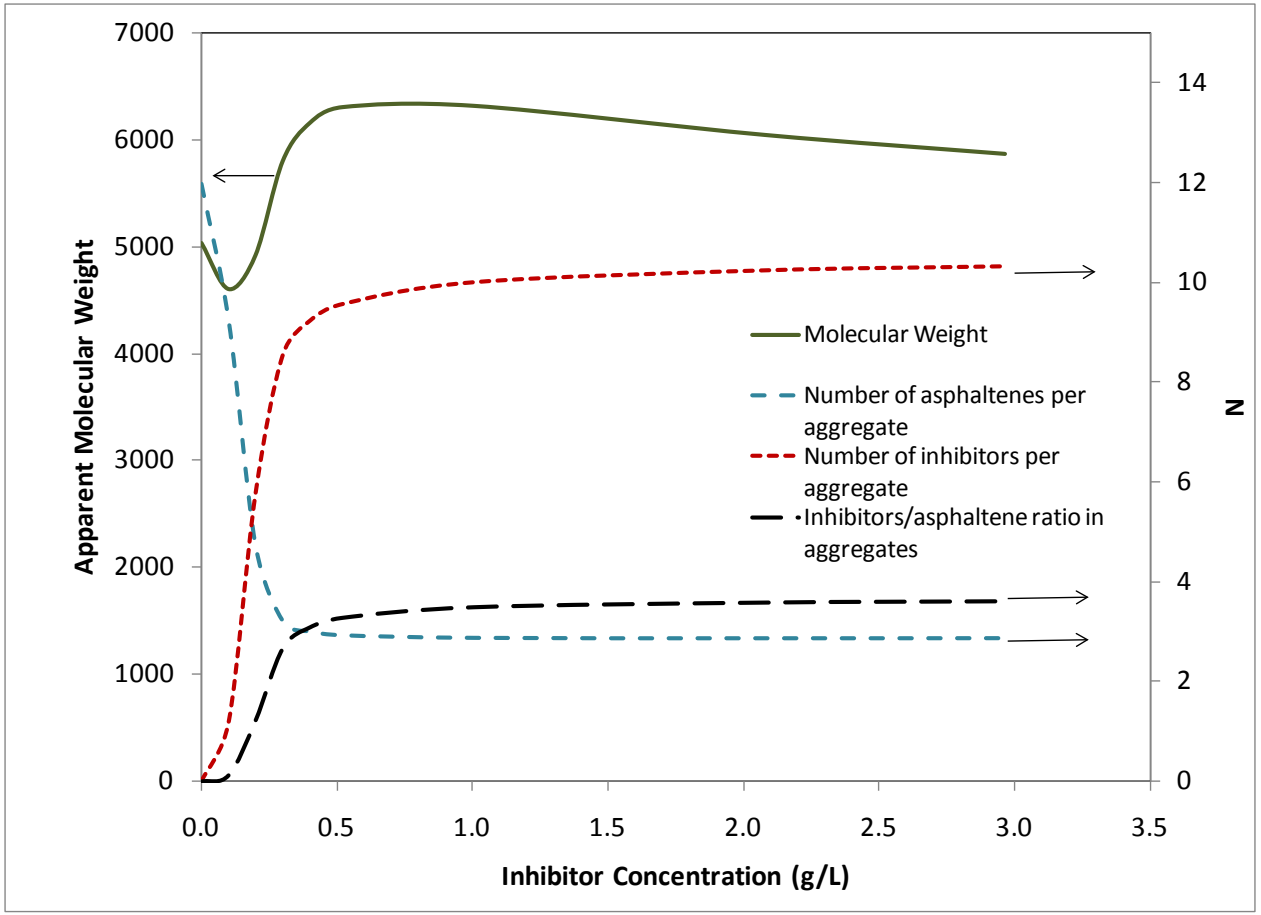




Specific factors related to asphaltene and inhibitor characteristics

- ✓ Strength of interactions between inhibitor's head and asphaltene active site.
- ✓ Strength of interactions between inhibitor's heads.
- ✓ Area occupied by inhibitor's tail at the interface.
- ✓ Solubility and size of polyaromatic rings.
- ✓ Number of active sites per asphaltene molecule.

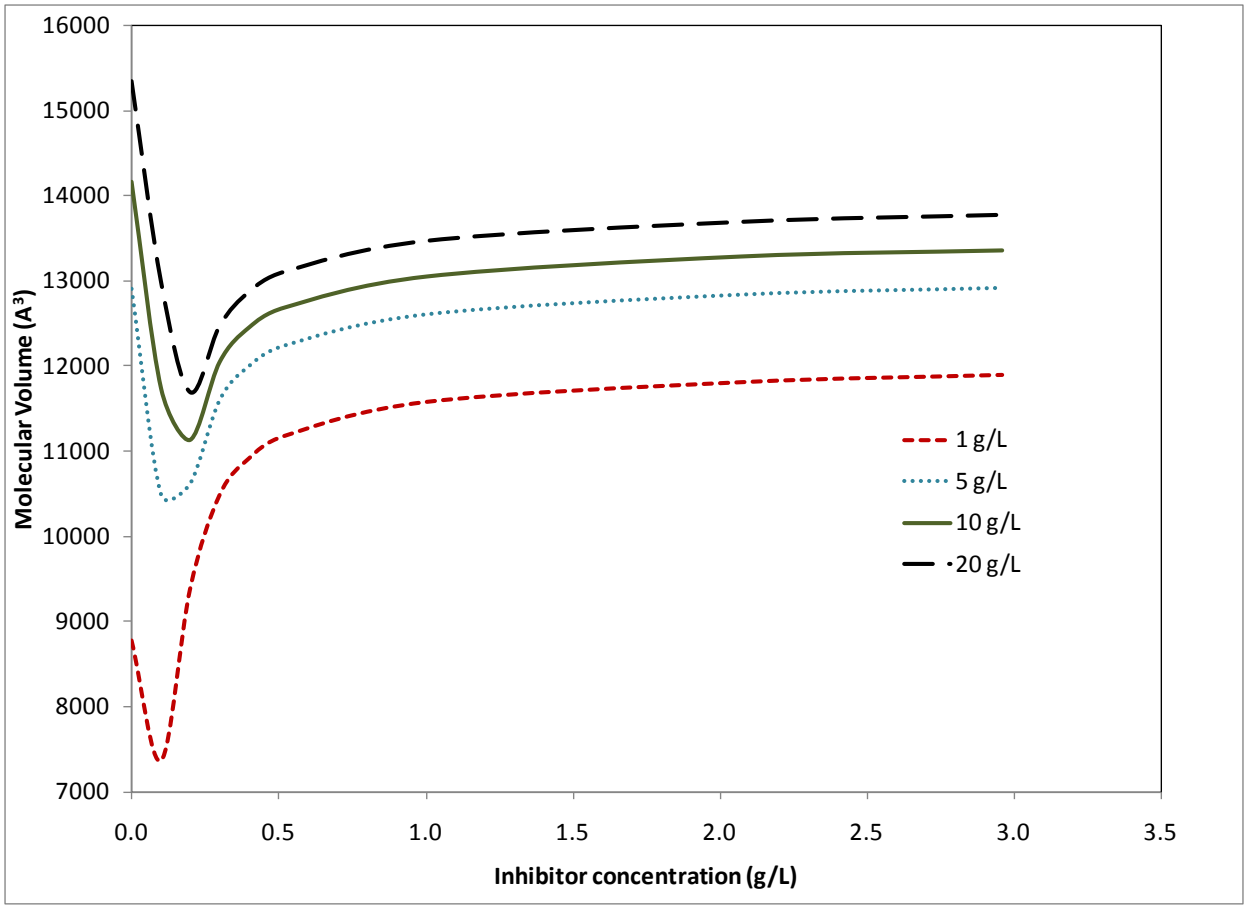
Effect of inhibitor on aggregate size



System: $A_6(C_7)_3$ in toluene. Asphaltene Concentration: 20 g/L

Apparent Molecular Weight measurements can be misleading about aggregate size distribution.

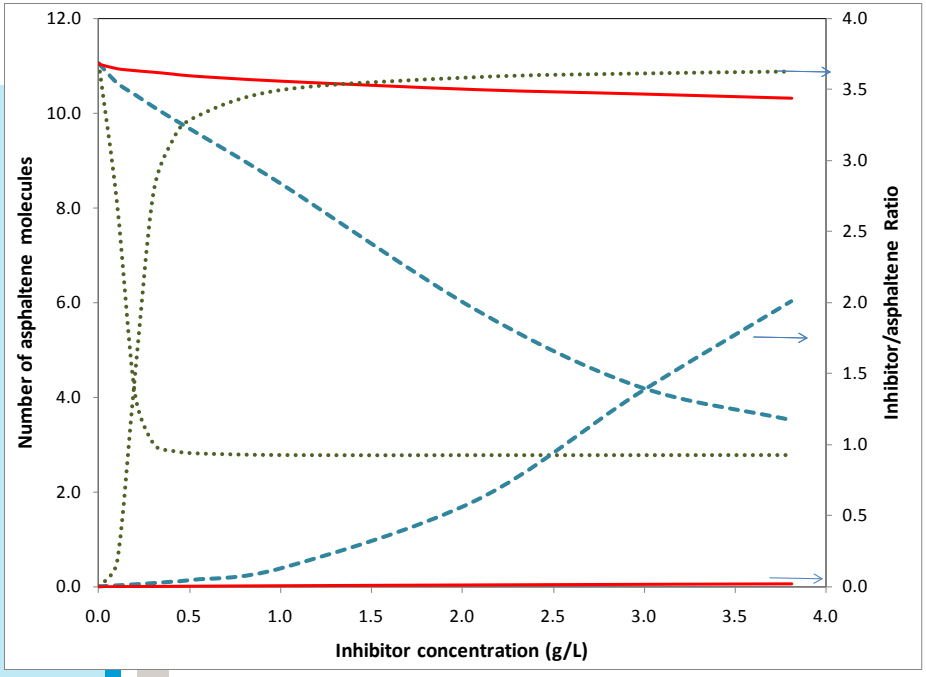
Effect of inhibitor on aggregate size at different asphaltene concentrations

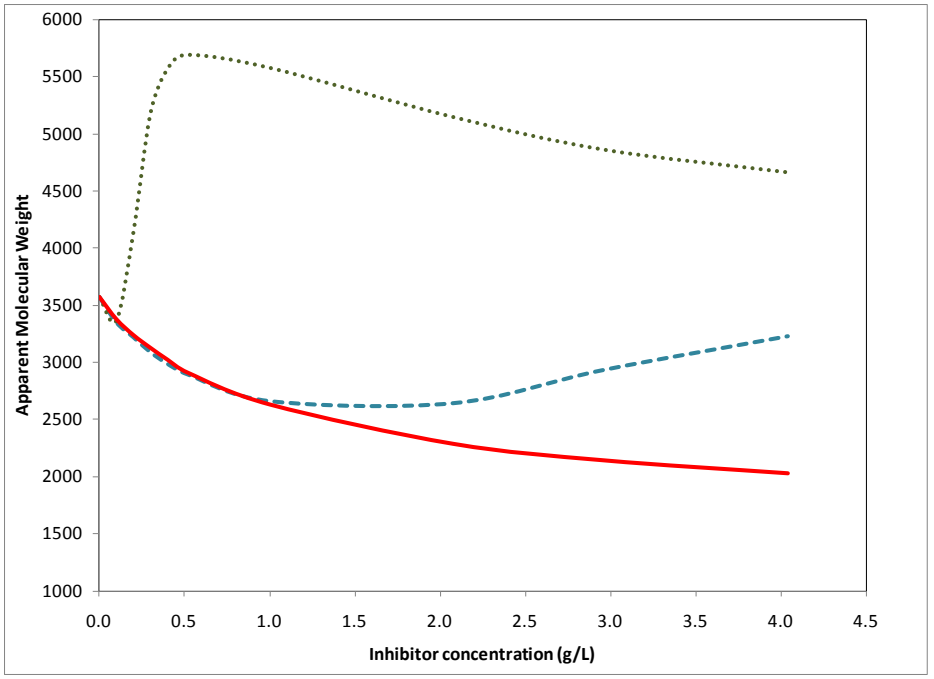


System: $A_6(C_7)_3$ in toluene.

Depending on the relative asphaltene and inhibitor concentrations, aggregates could be larger, smaller or more or less the same size than the original aggregates

Effect of inhibitor on aggregate size depending on the strength of inhibitor-asphaltene interactions





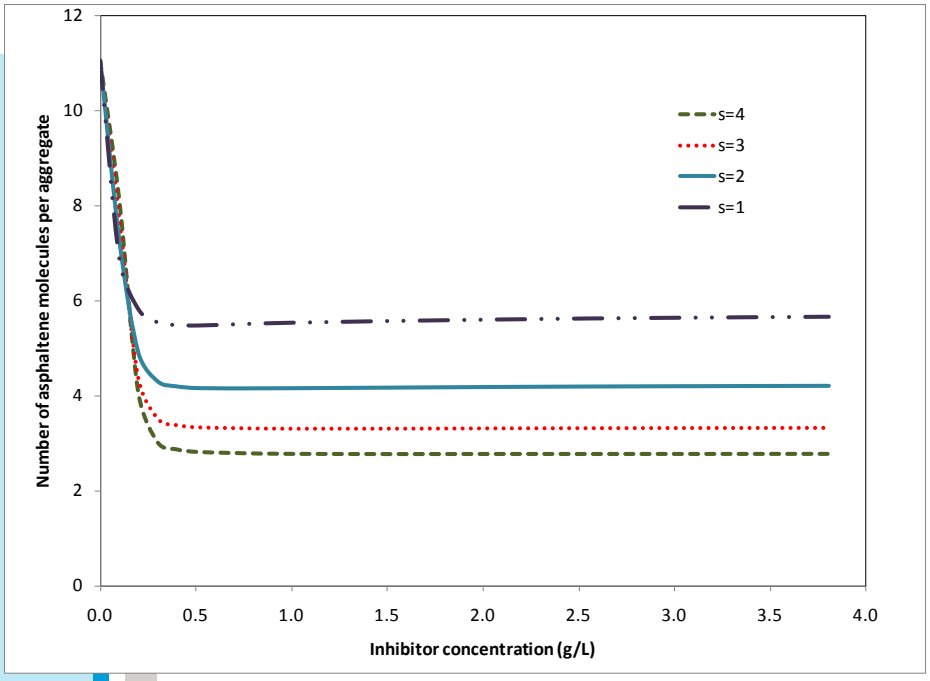
$\cdots\cdots\Delta G_{site\text{-}inhibitor} < \Delta G_{inhibitor\text{-}inhibitor}$ $\quad$ $- - - - - - - \Delta G_{site\text{-}inhibitor} = \Delta G_{inhibitor\text{-}inhibitor}$

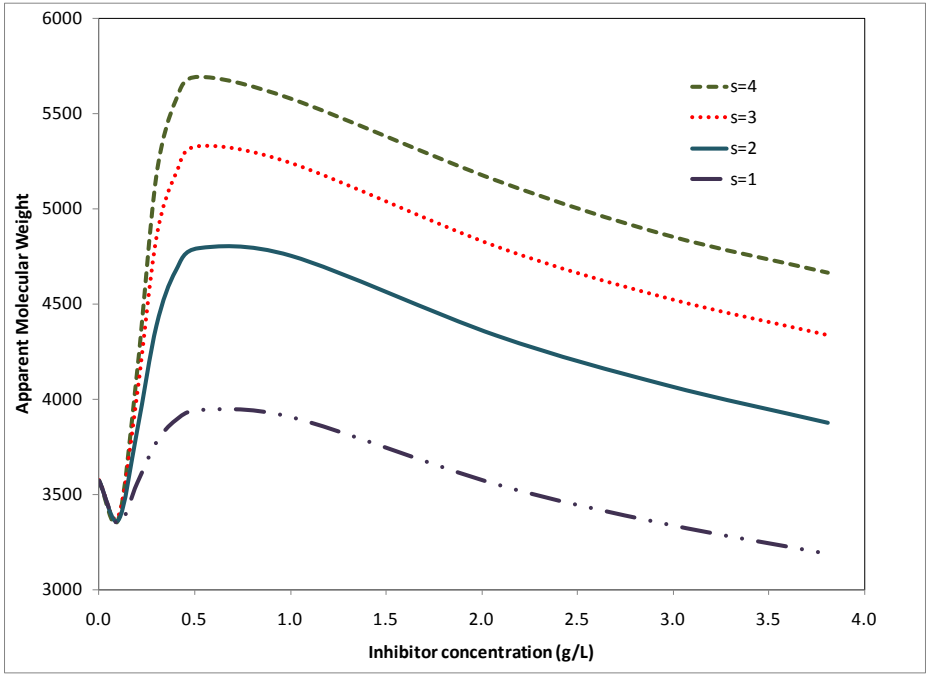
$\_\_\_\_\_\Delta G_{site\text{-}inhibitor} > \Delta G_{inhibitor\text{-}inhibitor}$

System: $A_6(C_7)_3$ in toluene. Asphaltene Concentration: 10 g/L

The minimum in molecular weight moves at higher inhibitor concentrations as the interaction energy between inhibitor and asphaltene site is less favorable.

Effect of inhibitor on aggregate size depending on the number of active sites in asphaltenes.

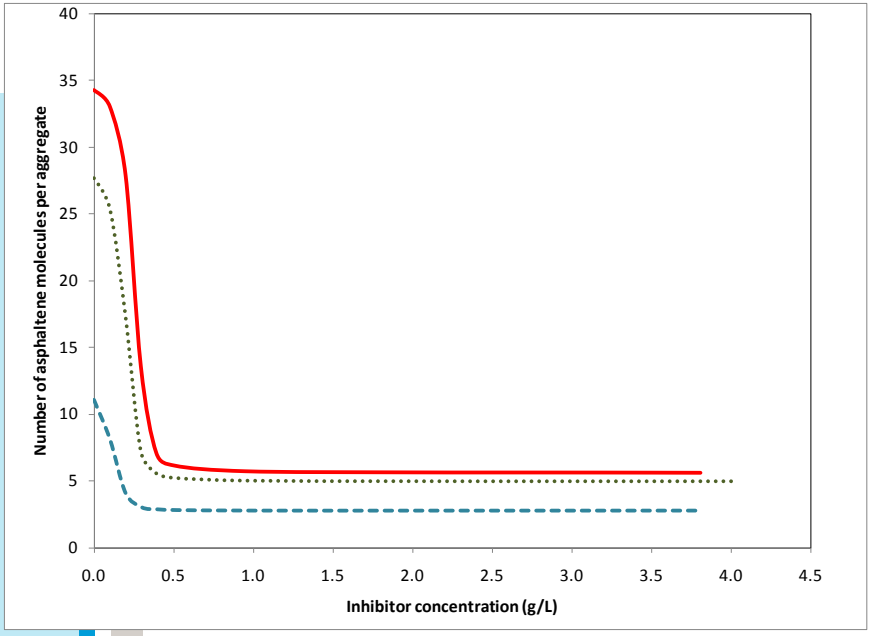


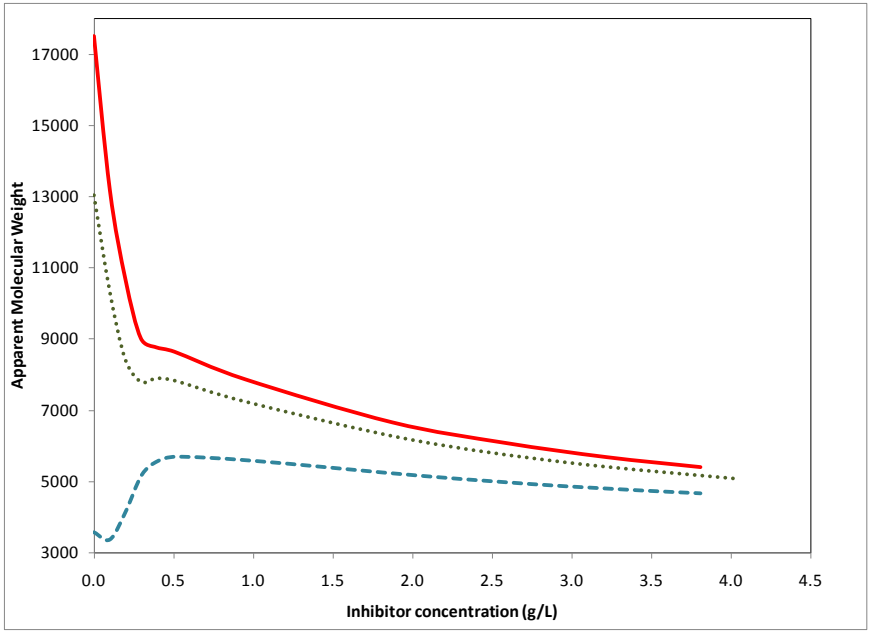


System: $A_6(C_7)_3$ in toluene. Asphaltene Concentration : 10g/L

The decrease in the number of active sites in the asphaltene decreases the effectiveness of the inhibitor to reduce asphaltene aggregation.

Effect of inhibitor on aggregate size depending on the polyaromatic ring characteristics.



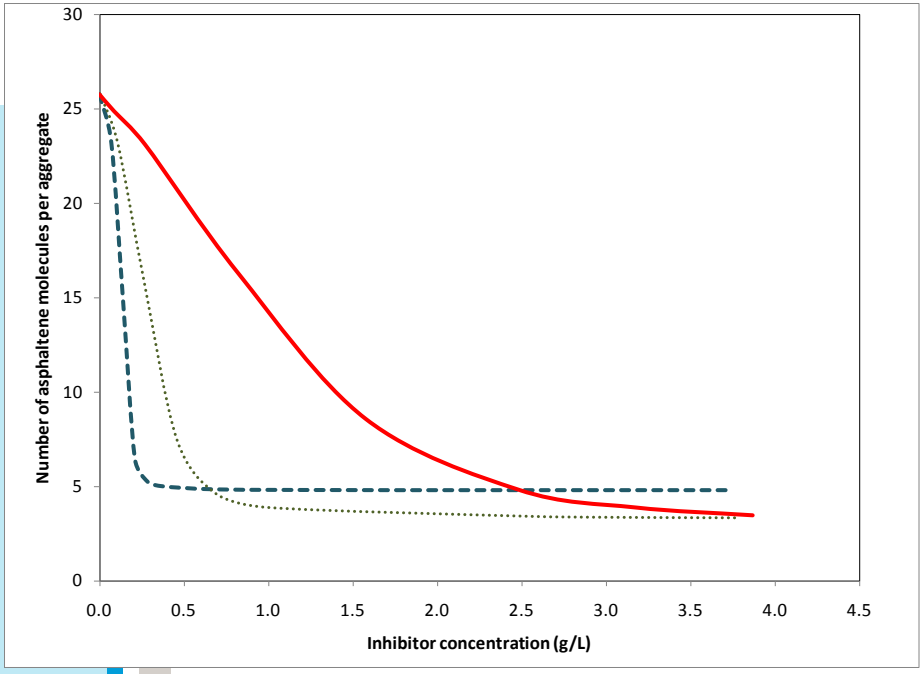


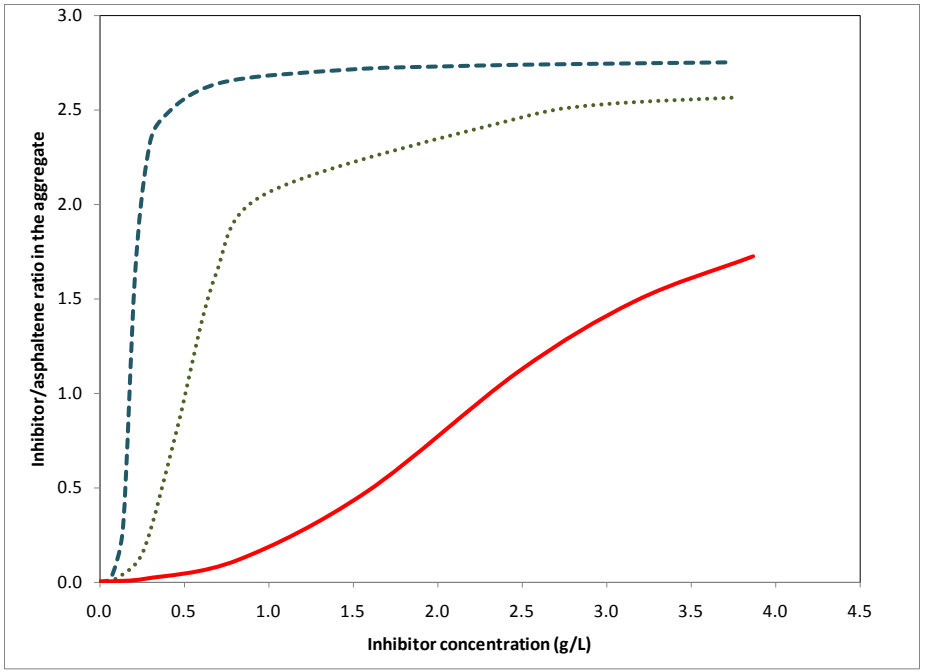
----$A_6(C_7)_3$ .....$A_7(C_7)_3$ ___$A_8(C_7)_3$

System: Toluene. Asphaltene Concentration : 10g/L

The efficiency of the inhibitor decreases as the asphaltenes tend to form larger aggregates.

Effect of inhibitor on aggregate size depending on the inhibitor tail characteristics. Area occupied by tails.



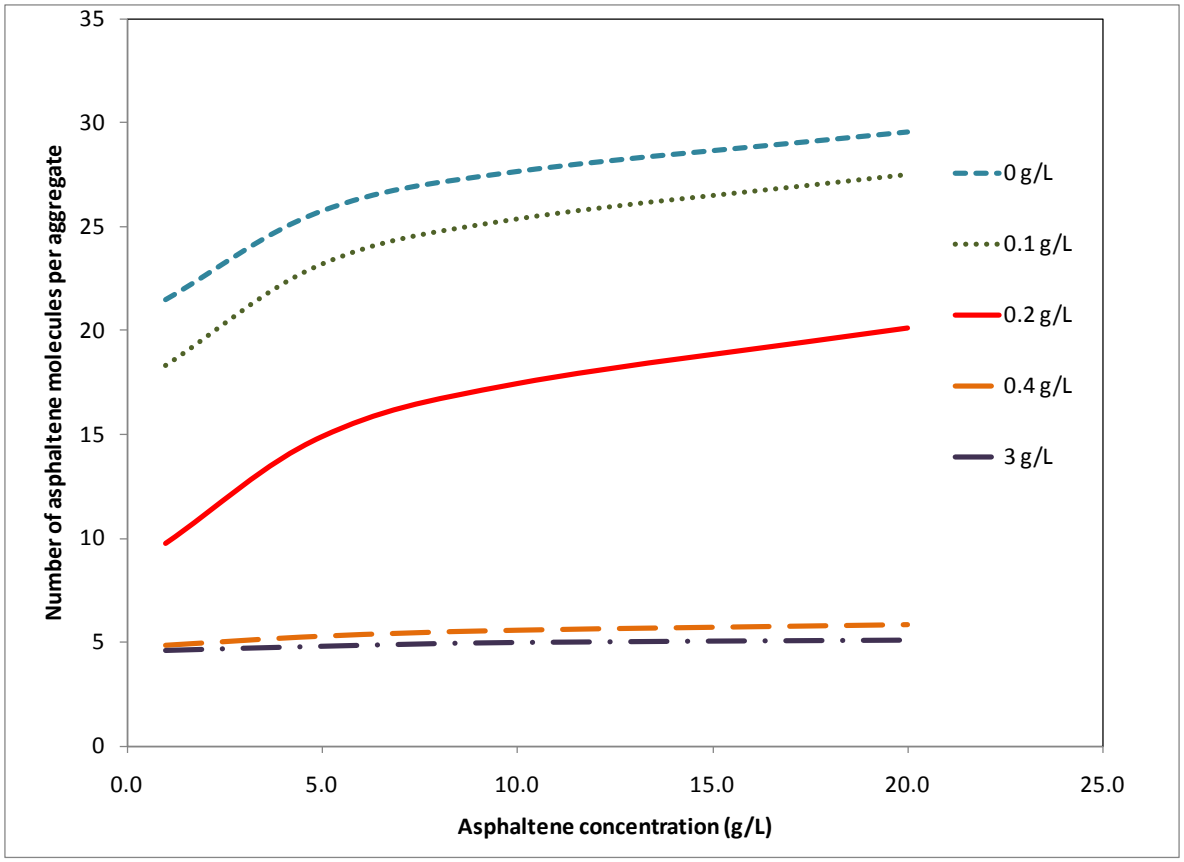


Tail areas at the interface: ---- ACH_2 ..... $2ACH_2$ ___ $3ACH_2$

System: $A_7(C_7)_3$ in Toluene. Asphaltene Concentration : 5g/L

The increase of the area occupied at the interface decrease the number of inhibitors needed to reach the same deaggregation level.
This area also affects the inhibitor self aggregation which occurs at large concentrations as the area increases.

Effect of asphaltene and inhibitor concentration



System: $A_7(C_7)_3$ in Toluene. Asphaltene Concentration : 5g/L

There is an optimum concentration for the inhibitor. Addition of more inhibitor after a certain point does not improve deaggregation of asphaltenes.

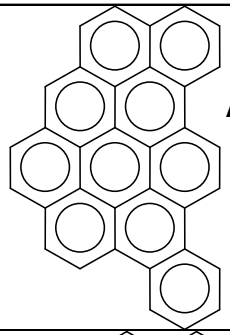
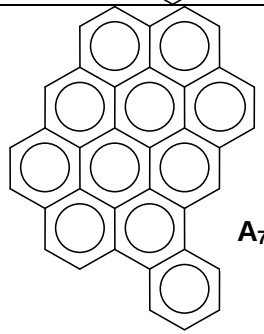
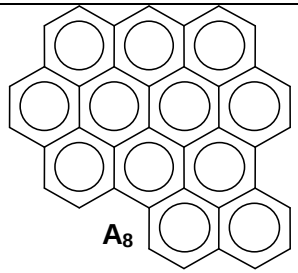
Conclusions

- ✓ By including specific factors related to asphaltenes and inhibitor characteristics, the model allows a rationalization of different aggregation behaviors observed for asphaltenes in the presence of inhibitors.
- ✓ The model predicts that there is a optimum inhibitor concentration for asphaltene aggregation that depends on a complex interplay between asphaltene and inhibitor characteristics.

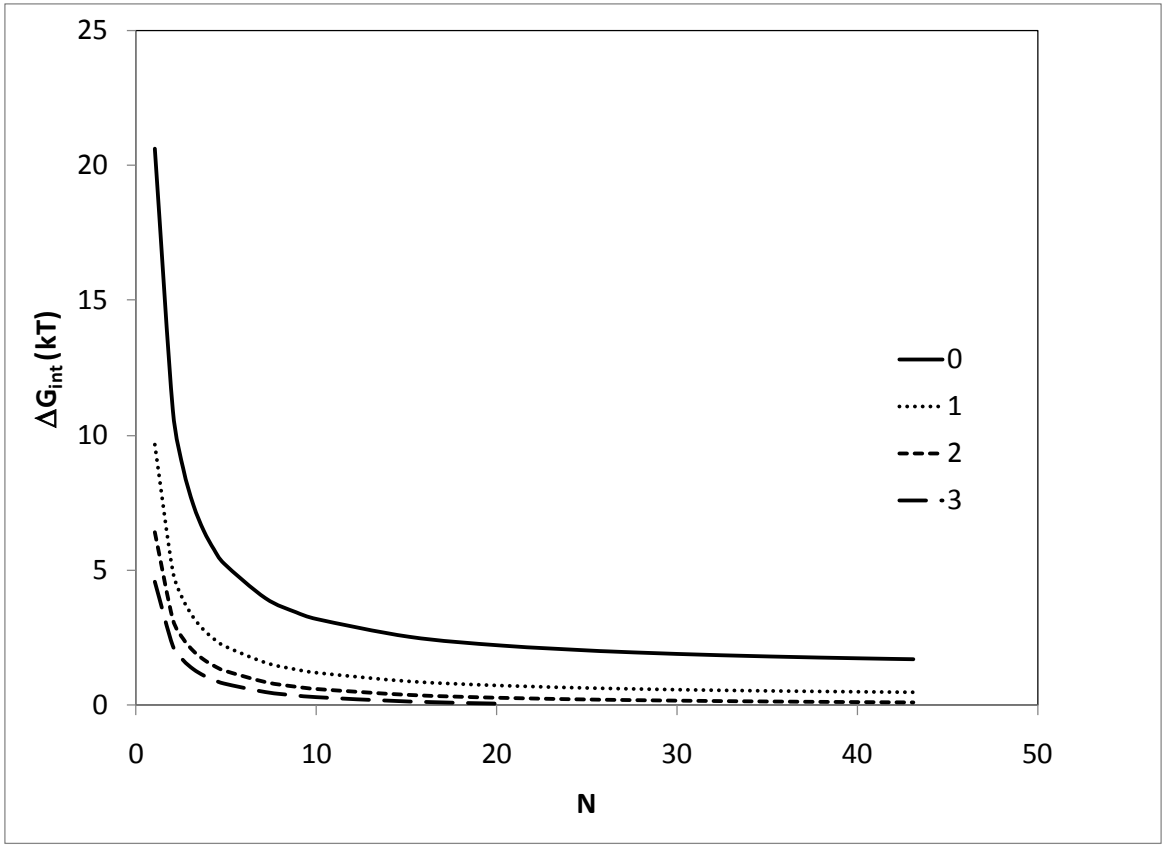
THANK YOU

Questions?

Properties of the polyaromatic moieties

Molecule	Melting Temperature (^oC)	Enthalpy of fusion (KJ/mol)	Molar Volume (cm^3/mol)	Solubility Parameter ($MPa^{0.5}$)
 A_6	571	29.8	409	24.5
 A_7	649	22.9	423	25.2
 A_8	748	21.7	437	26.1

Effect on number of inhibitors per aggregate on Free energy: Interfacial Free Energy



Effect on number of inhibitors per aggregate on Free energy: Steric Free Energy