McBain Medal Lecture: Lubricant Additives – Non Aqueous Colloids

Peter J. Dowding

Performance you can rely on.

Infineum

Overview

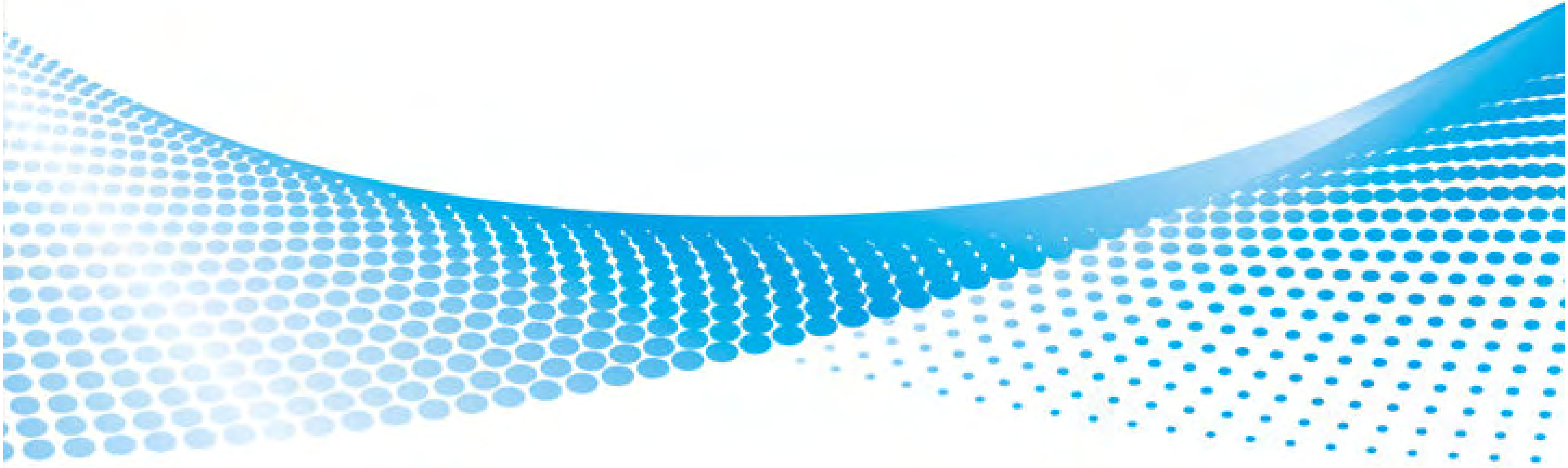
- Micron-Sized Aqueous Dispersions - Bristol University
  - Suspension polymers as chromatographic supports
  - Emulsification via cross-flow membrane
  - Polymerisation using a novel tubular reactor

- Non-Aqueous Dispersions - Infineum
  - Introduction to Additives/ Detergents
  - Interaction studies of detergent particles:
    - Mechanism of acid neutralisation
    - Interaction of detergents with water
    - Surfactant exchange/ competitive adsorption

- Conclusions/ Acknowledgements

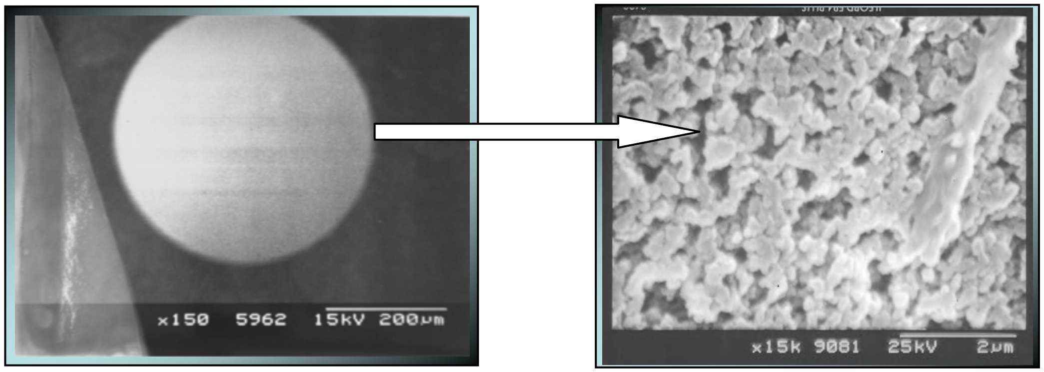
Novel Emulsification

For Production of Suspension Polymer Beads

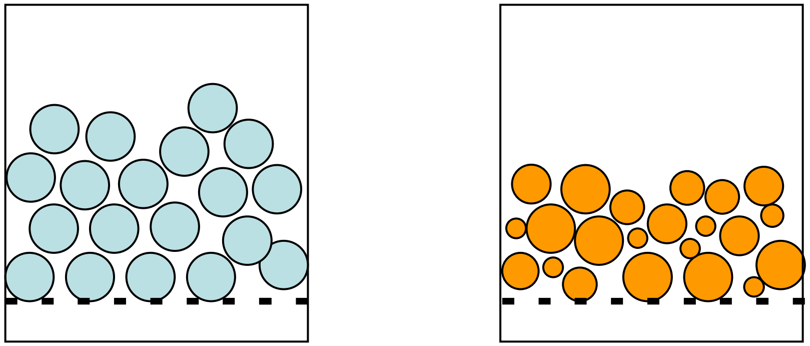


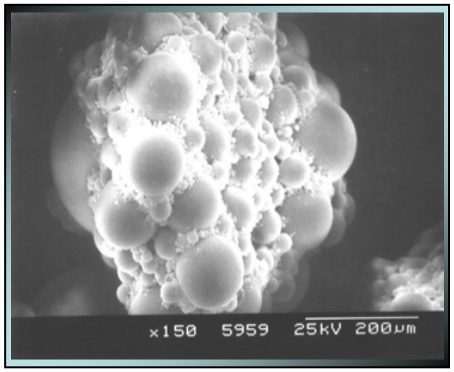
Suspension Polymers as Chromatographic Supports

- Porous, beaded copolymers produced by suspension polymerisation are commonly used in separation media (particle size ~ 100 µm)
- Porosity increases surface area



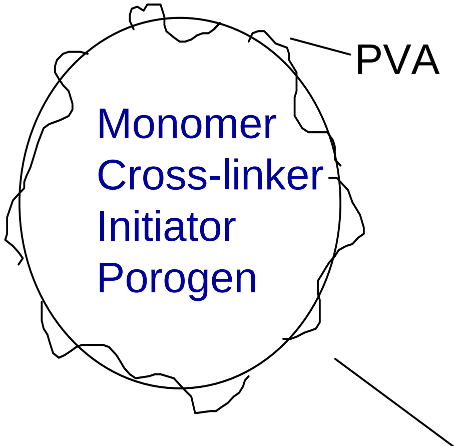
- Require a narrow size distribution to avoid pressure drop, generally achieved by (wasteful) sieving of the polymer

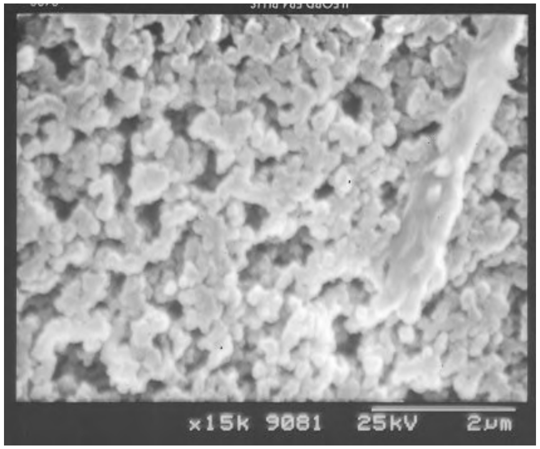




Suspension Polymerisation

Emulsion Droplet





Monomer is converted directly into polymer within the droplets

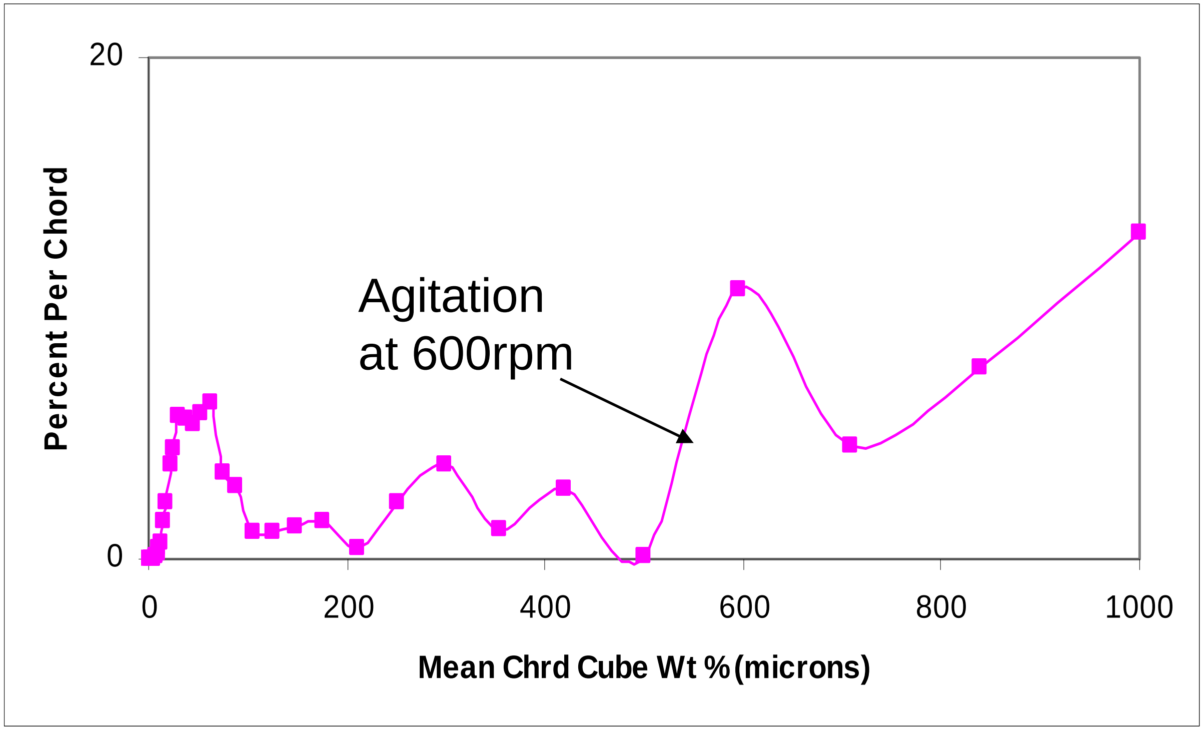
Polymerisation proceeds leaving pores in the bead

Polymer Bead

- The size distribution of the final particles is determined by the size distribution of the emulsion and a balance between coalescence and break-up of the polymer droplets during polymerisation.

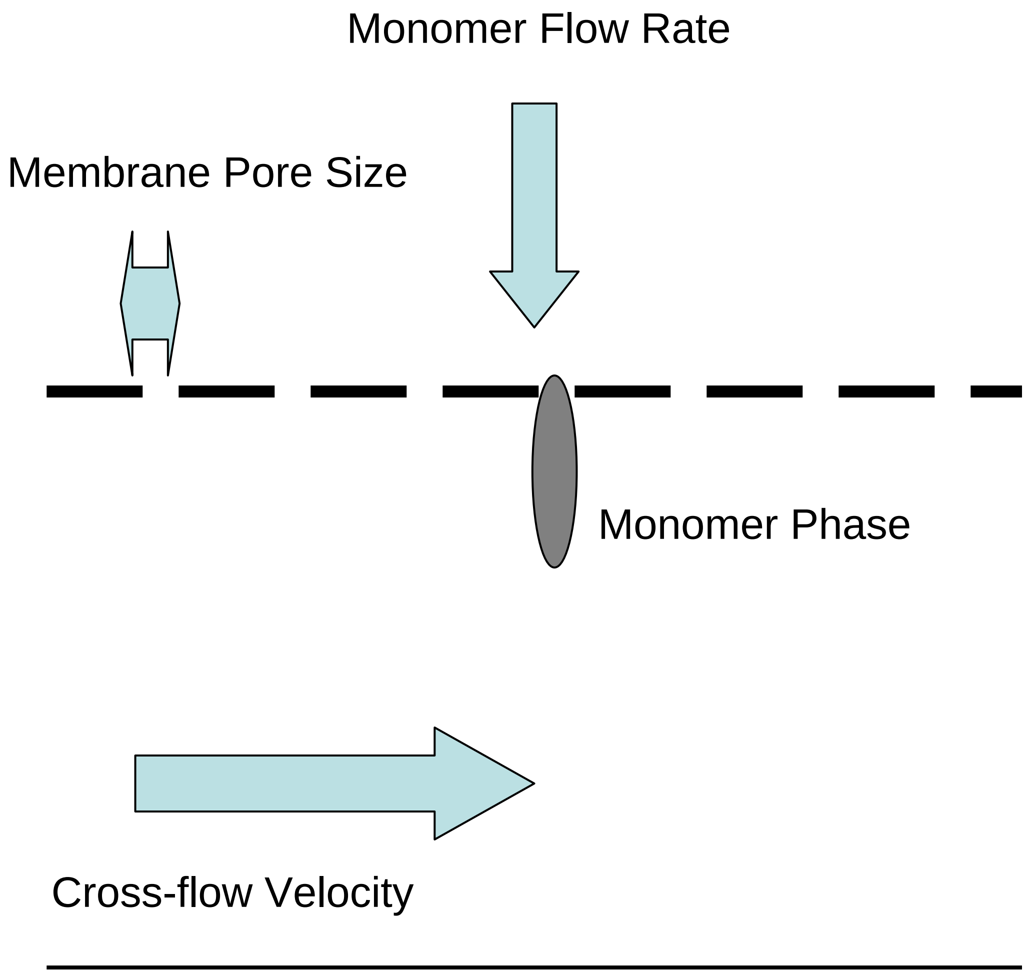
Droplet Size Distribution During Emulsification by Shear

- Monomer phase: Styrene/ Divinyl Benzene/ 4-methyl-2-pentanol
- Size distribution determined by laser back-scattering (Lasentec FBRM)



- Emulsification by shear results in wide polydispersity

Novel Emulsification: Cross-Flow Membrane

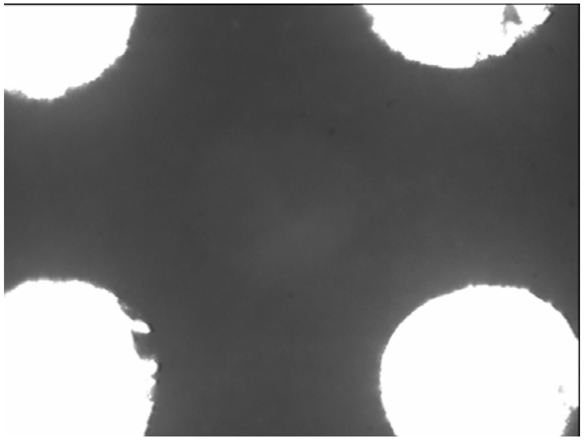


Monomer Flow Rate

Membrane Pore Size

Monomer Phase

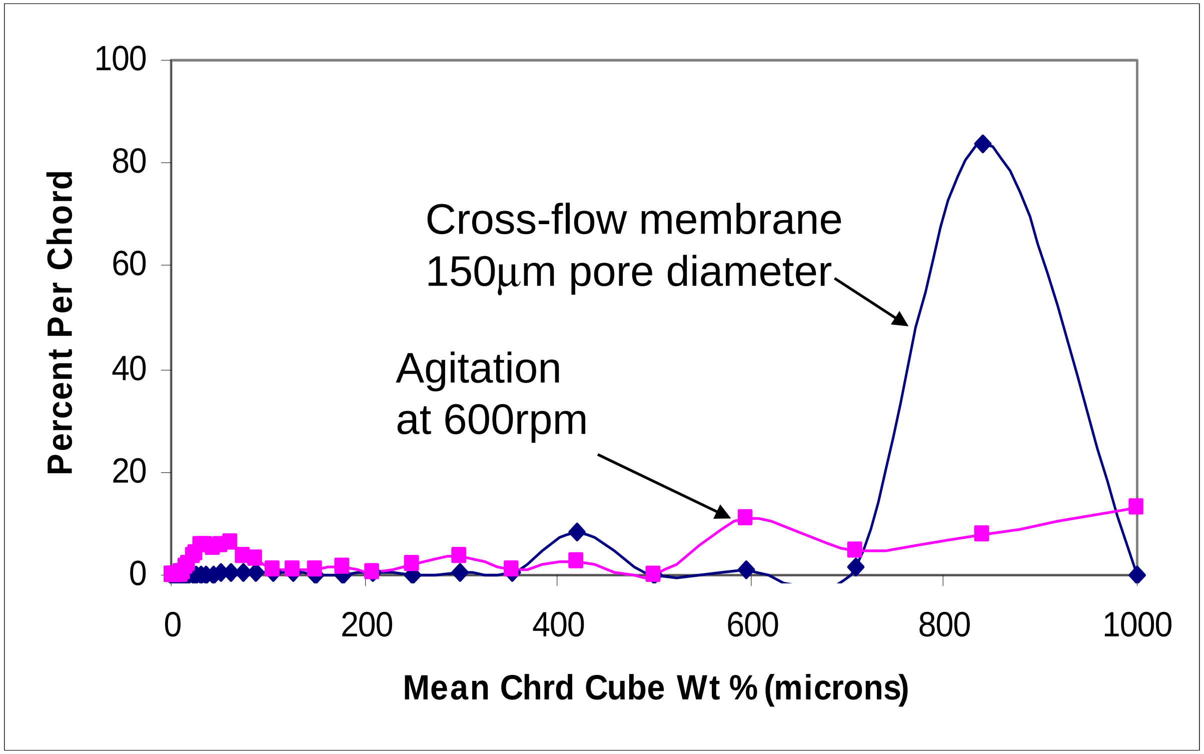
Cross-flow Velocity



150µm laser drilled holes

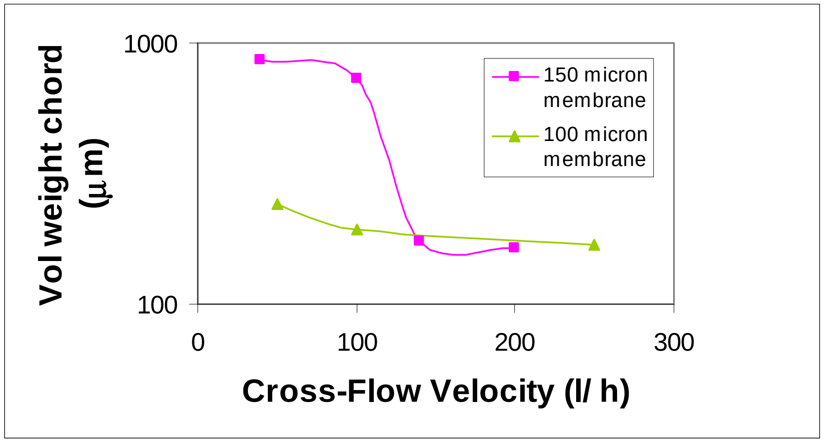
Emulsion Droplet Size Distribution

- Emulsification using crossed flow membrane results in a much narrower size distribution (some satellite droplets)



Effect of Flow rates & Membrane Size

- Variation in cross-flow velocity/ membrane pore size
  - At fixed monomer flow rate (300 ml h^{-1})

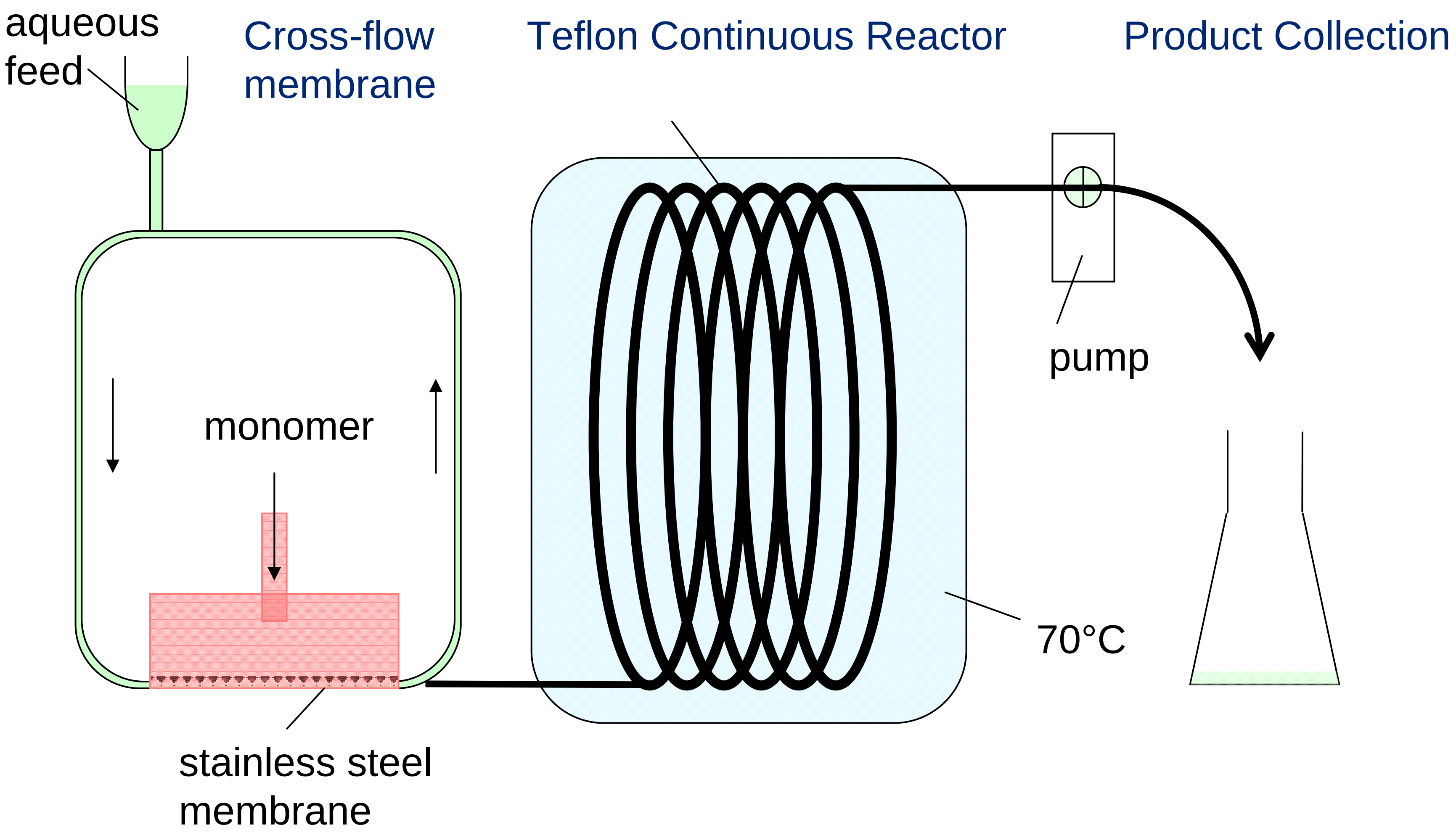


- Variation in monomer flow rate
  - At fixed cross-flow rate (50 l h^{-1}) for 100 µm membrane

Monomer flow-rate (ml h^{-1})	400	300
Ave. vol. wt. size (µm)	380	240

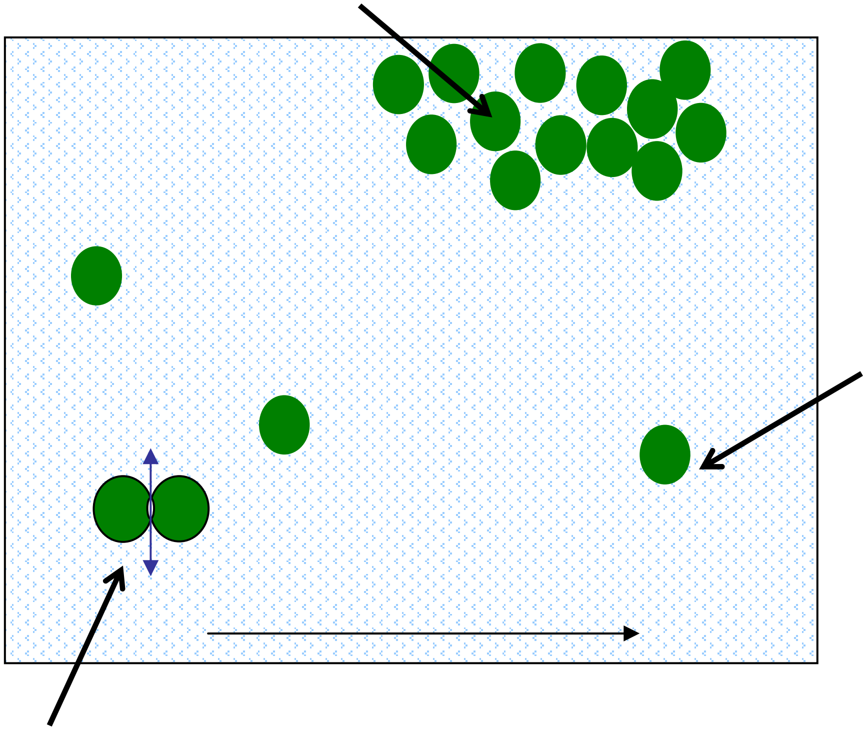
- Control of droplet size is possible

Continuous Production Set-up



Droplet Instability in Continuous Reactor

- ***Droplet Creaming*** due to density differences between droplet and continuous phase
  - Overcome by density matching using a denser (brominated) porogen

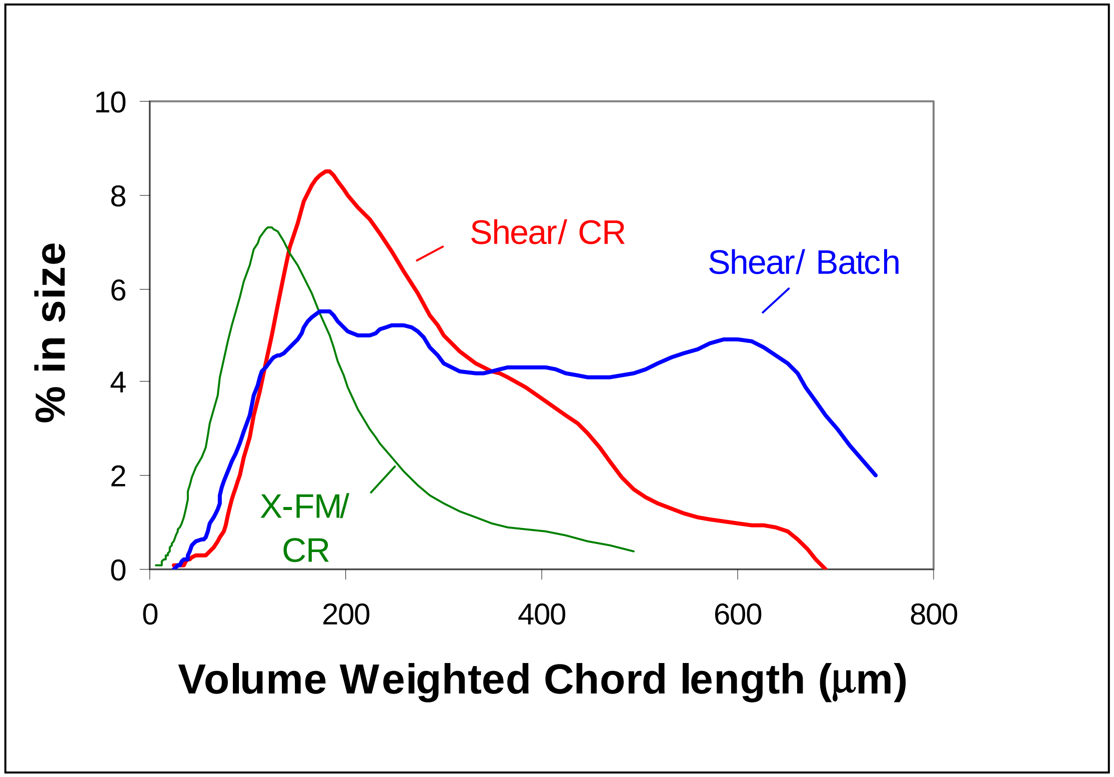


- ***Break-up of Drops:***
  - Maximum force is at 45° to flow
  - Break-up is reduced by high interfacial tensions and high particle viscosity

- ***Coalescence rate*** is controlled by liquid drainage from between droplets:
  - Rigidity of the surface controls damping of instabilities
  - Increasing droplet viscosity increases rigidity of surface

Polymerisation in Continuous Reactor/ Batch

- Monomers: glycidyl methacrylate, divinyl benzene, with PS present
- Reaction time: (from kinetic studies) ~4 hours. pore radius: ~31 nm



- Peak width at half height: Shear/ Batch ~600 µm, Shear/ C.R. ~230µm, X-FM/ C.R. ~150µm

Conclusions

- Emulsification using cross-flow membrane improves emulsion size distribution and reduces droplet breakage, due to lower shear
- This combined with polymerisation in a tubular reactor can reduce the polydispersity of beads (compared with a batch reaction), removing the need for product sieving
- The reactor wall should have a low surface energy (*e.g.* Teflon)
- By careful control of the recipe: increase in droplet viscosity and density matching of phases, fouling of the reactor does not occur

Lubricant Additives

Surfactant Stabilised Particles

Functions of Additives

- Minimise Destructive Processes
  - Oxidation
  - Friction and mechanical wear
  - Rust and corrosion
  - Shear

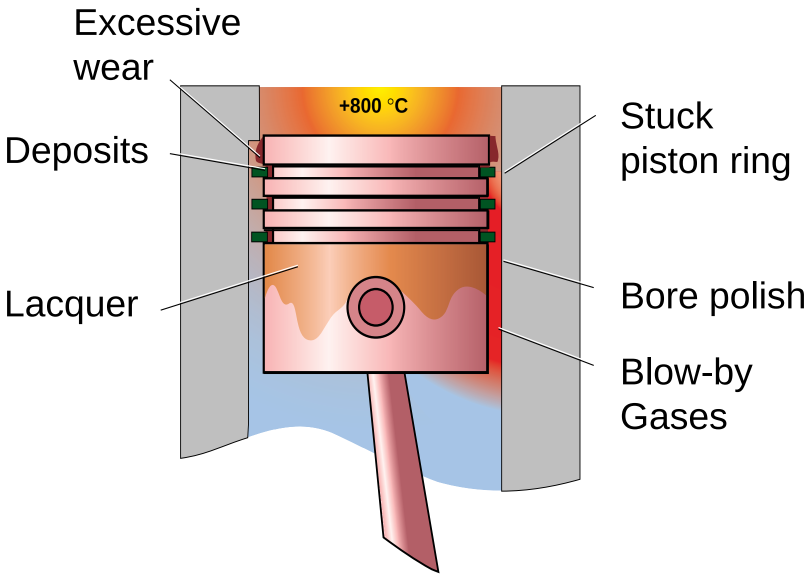
- Confer Beneficial Properties
  - Improved fuel economy
  - Extended drainage intervals
  - Reduced emissions

Consumers **Hardware**

Environment **Globalisation**

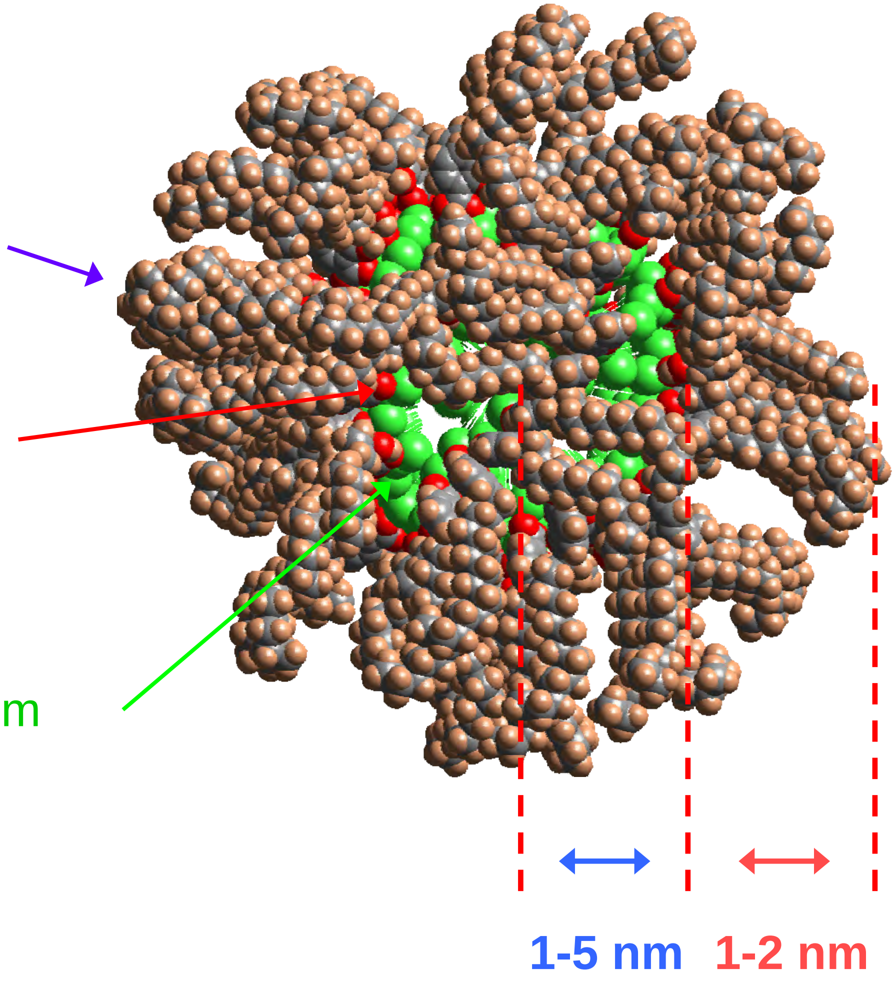
Functions of Detergents

- Neutralise acidic blow-by gases
  - Prevent corrosive wear
- Reduce lacquer, carbon and varnish deposits on pistons
  - Keep the engine clean
- In Marine Applications: Reduce formation of black sludge



- Challenge is to produce stable detergents, which are compatible with other additives and neutralise acids before they reach the walls of the cylinder

Structure of Detergents



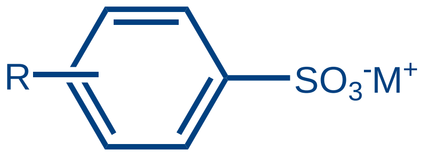
Steric stabilising surfactant layer - calcium salicylate (or sulphonate)

Surface layer of calcium hydroxide

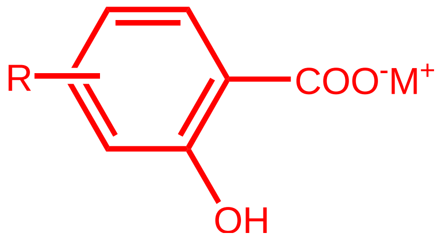
Inorganic calcium carbonate core

- (Base-containing) water-in-oil emulsions/ microemulsions have been described

Surfactants Used to Stabilise Detergents



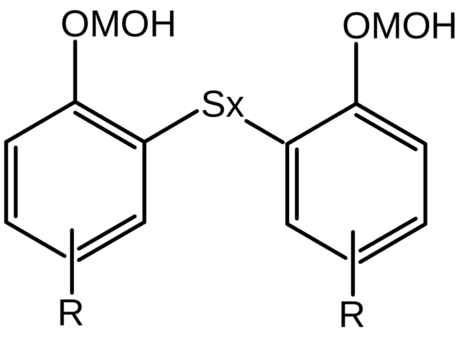
Alkyl Benzene Sulphonate



Alkyl Salicylate

M – Typically Mg or Ca

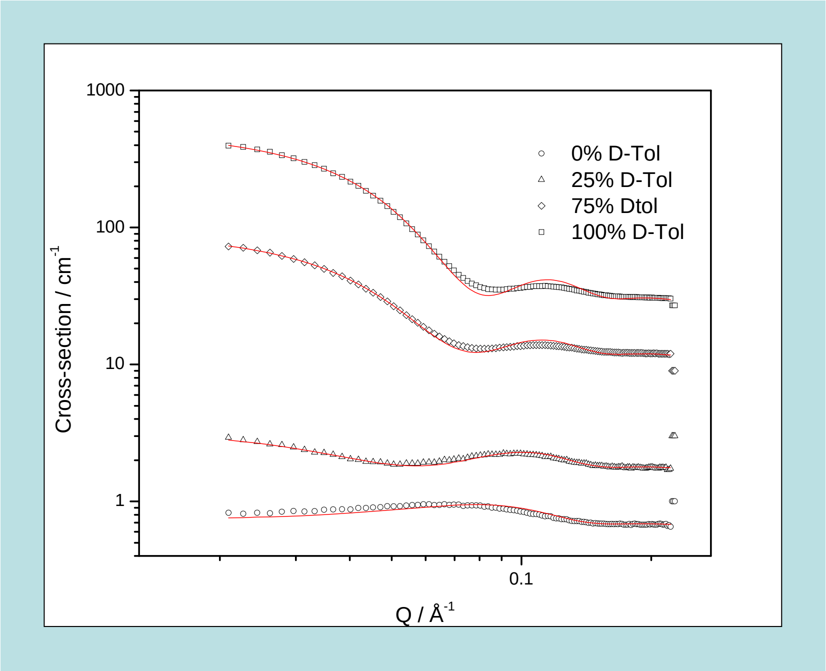
R – Typically > C_{12} linear or branched



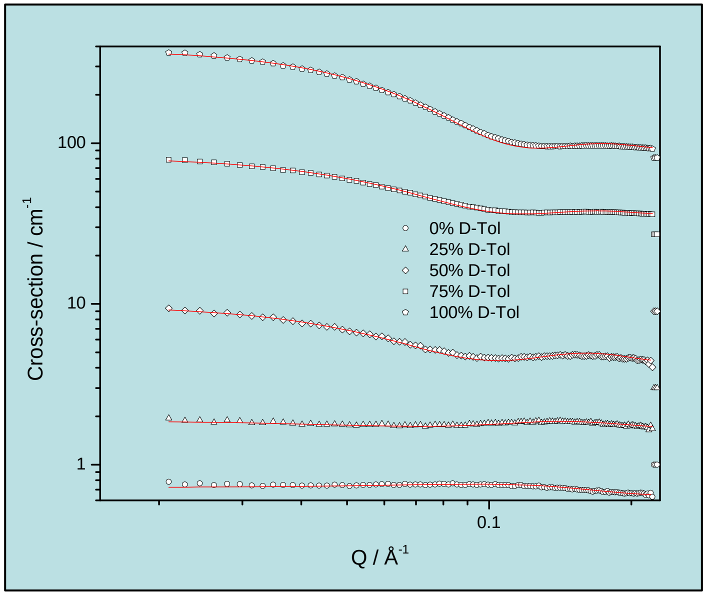
Phenates

SANS –Particle Sizing of Detergent Particles

Alkyl Benzene Sulphonate



Alkyl Salicylate



- Multiple contrast experiments:

Rcore = 28.3 Å
tshell = 16.7 Å
σ = 0.12

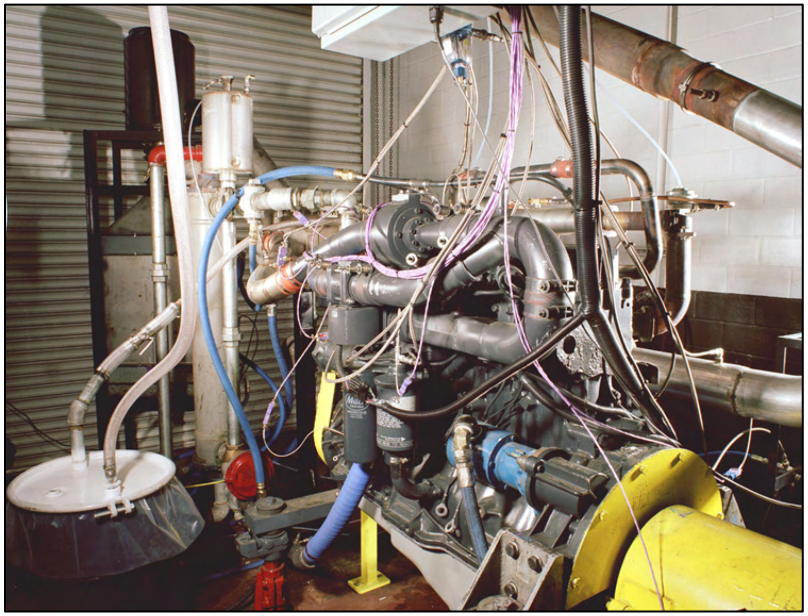
Rcore = 19.5 Å
tshell = 9.5 Å
σ = 0.12

- Particles produced on large scale (multi-hundred tonne batches)

Mechanism of Acid Neutralisation

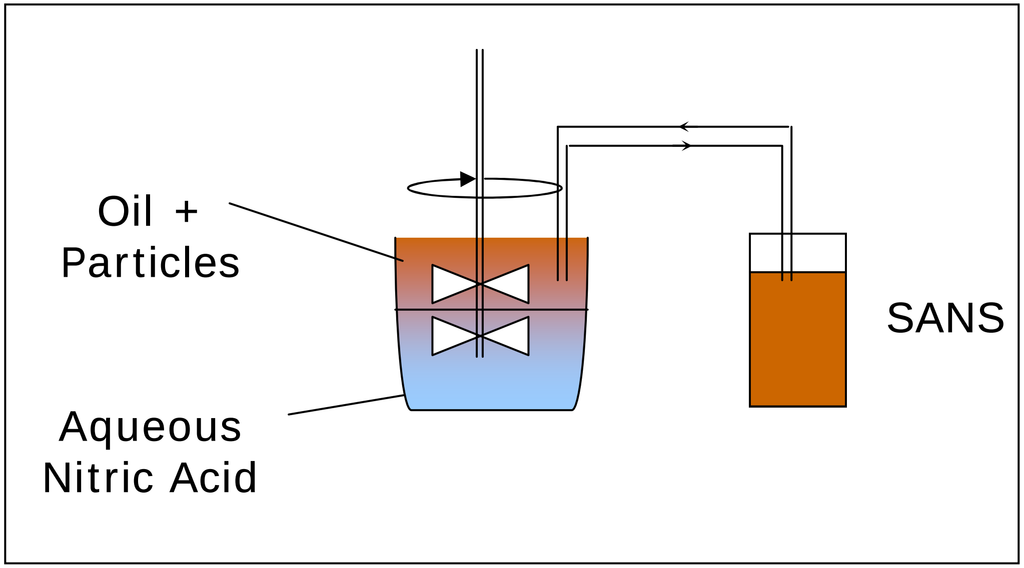
- Acids can enter the lubricant either via acidic “blow-by” gases or via oxidation of the base oil

- Exhaust gas recirculation is used in diesel engines:
  - To lower combustion temperature (increases levels of CO_2 and H_2O)
  - This results in reduced NO_x emissions
  - Can result in increased acid content entering the lubricant



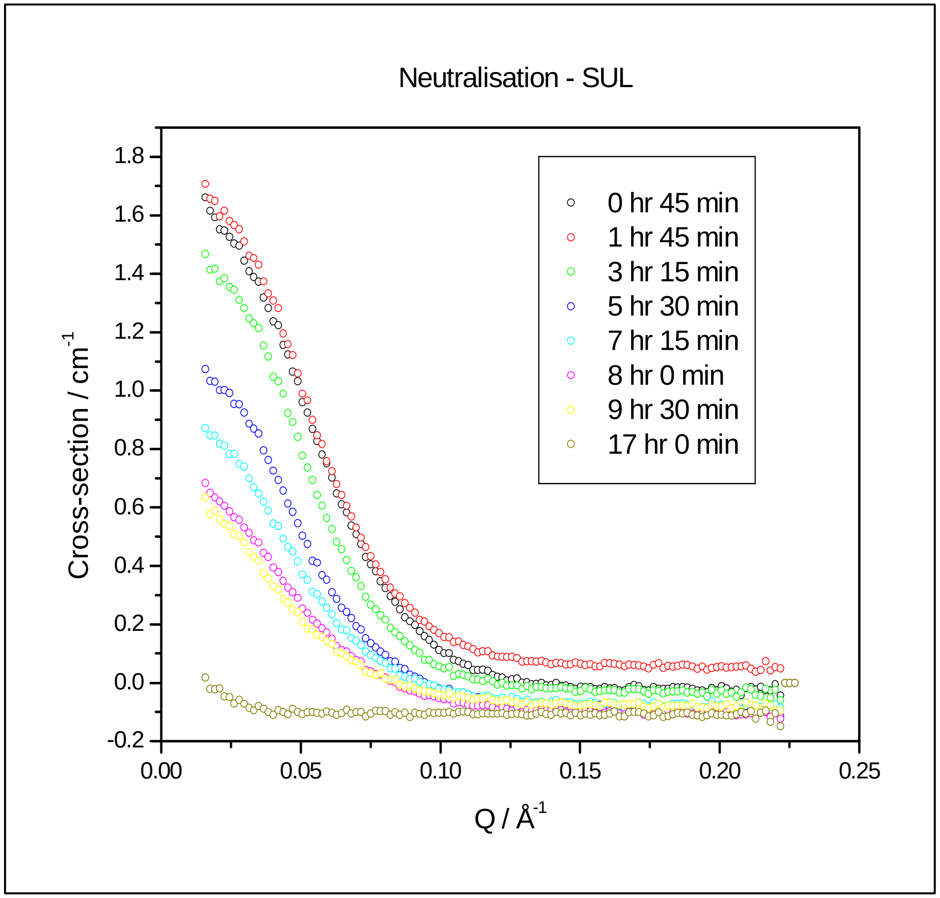
- Motivation to study the interaction of detergent particles with large emulsion droplets containing acid

Neutralisation Across an Unperturbed Interface



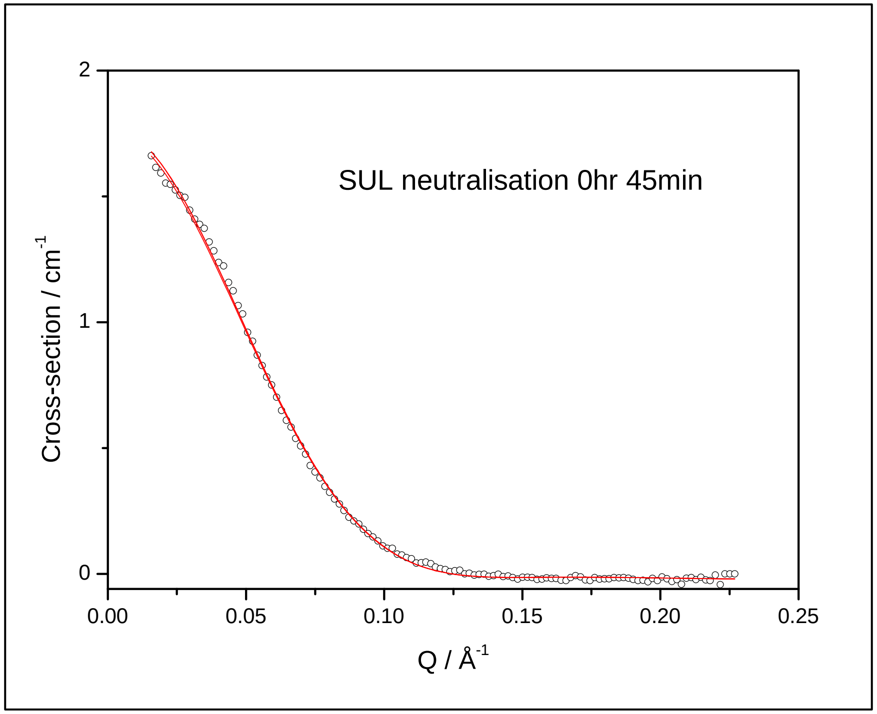
- Experimental setup:
  - Neutralisation across flat (stirred) interface
  - Excess acid present

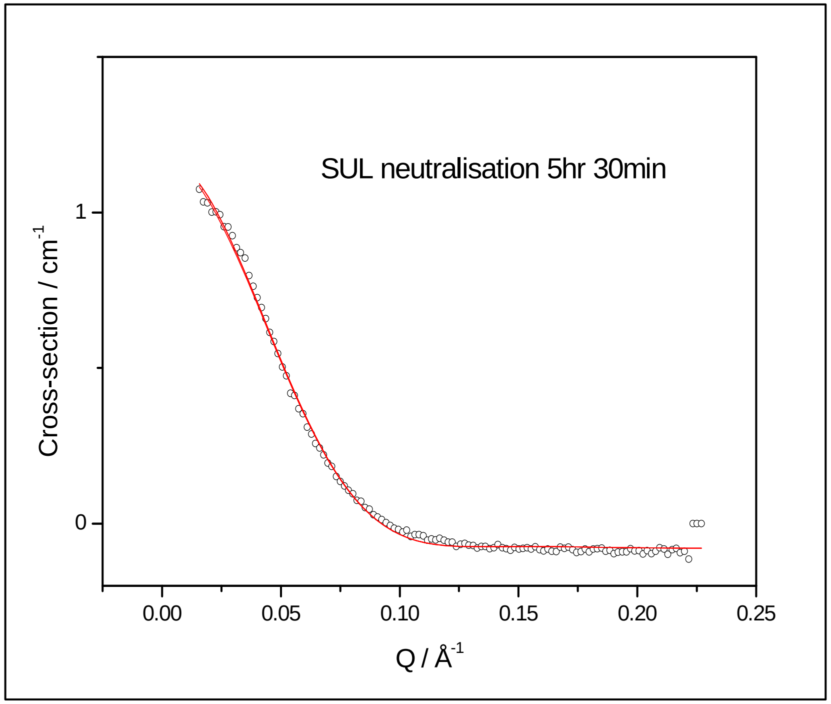
SANS – Sulphonate Neutralisation



- Measured I(Q)
- Particle size does not decrease
- Particle concentration falls

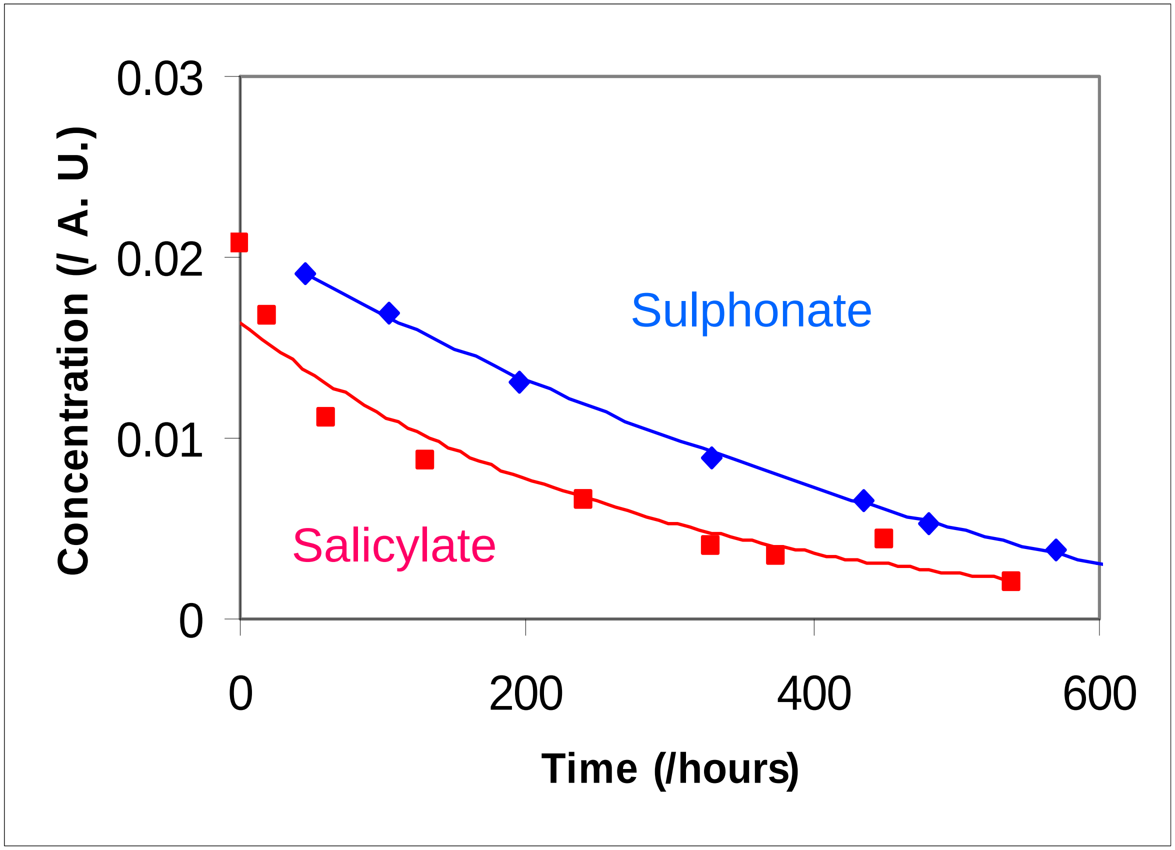
SANS – Sulphonate Neutralisation





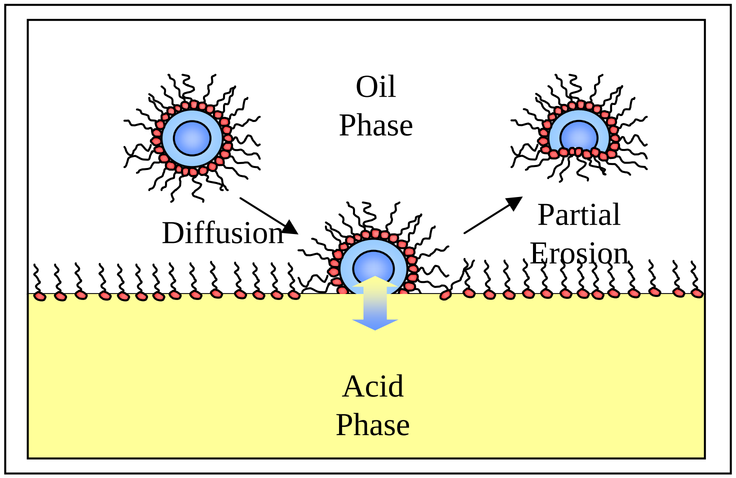
- Good fits to core-shell model (no significant attractive instabilities)

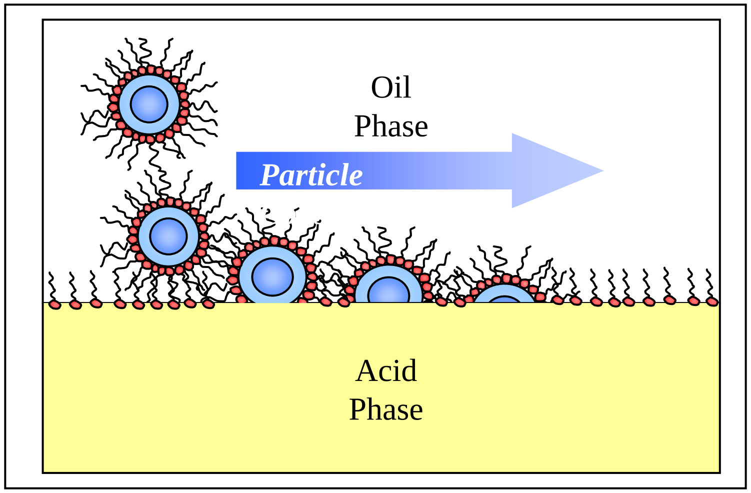
SANS – Acid Neutralisation



- SANS shows slow consumption of particles

SANS – Sulphonate / Salicylate Neutralisation

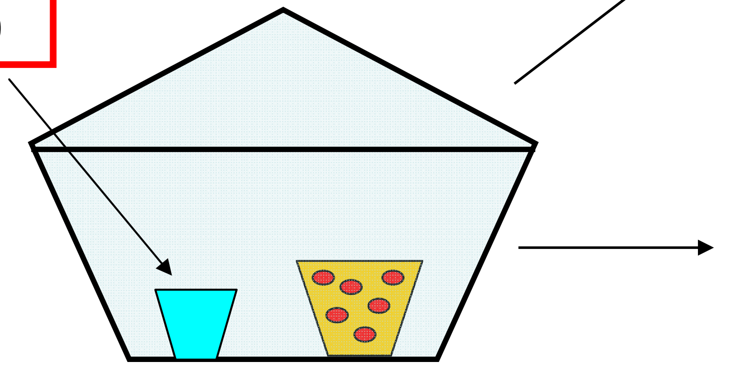




- Mechanism?
- SANS does not support partial erosion mechanism
- Particles appear to be adsorbed and rapidly consumed at interface

Motivation for Studying Interaction of Water

- Water is present in lubricants:
  - Trace water from synthesis of additives
  - Product of combustion of fuel
  - Product of acid neutralisation
- How does water interact with the detergent systems?
- Could this influence field performance?
- Expose samples of Detergent to a saturated vapour environment:



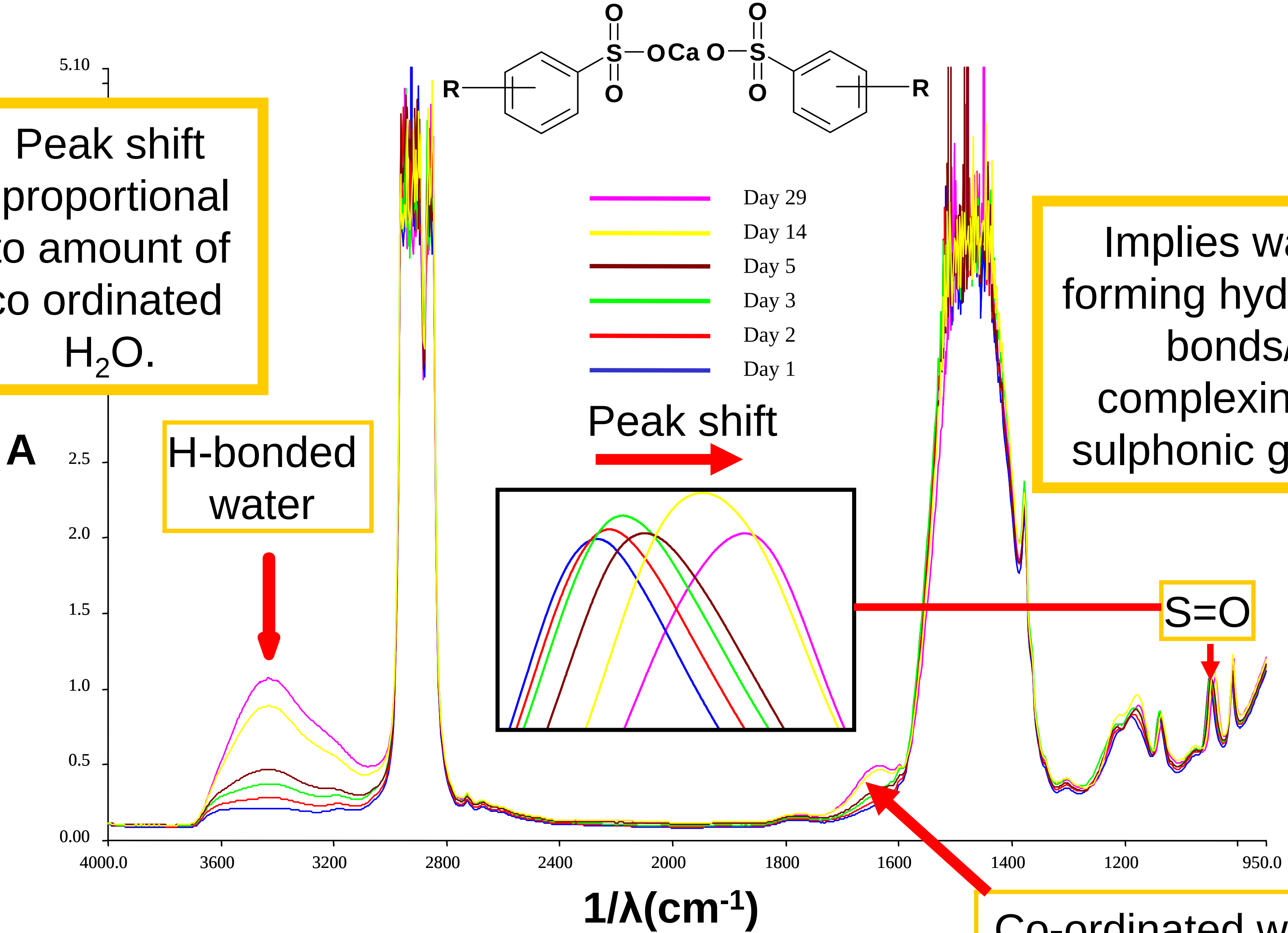
Open beaker of water (D_2O)

D_2O: SANS performed after 6 weeks

H_2O: FTIR spectrums taken over 6 weeks

Desiccator

FTIR-Spectra of Sulphonate in Contact with Water Vapour



Peak shift proportional to amount of co ordinated H_2O.

H-bonded water

Peak shift

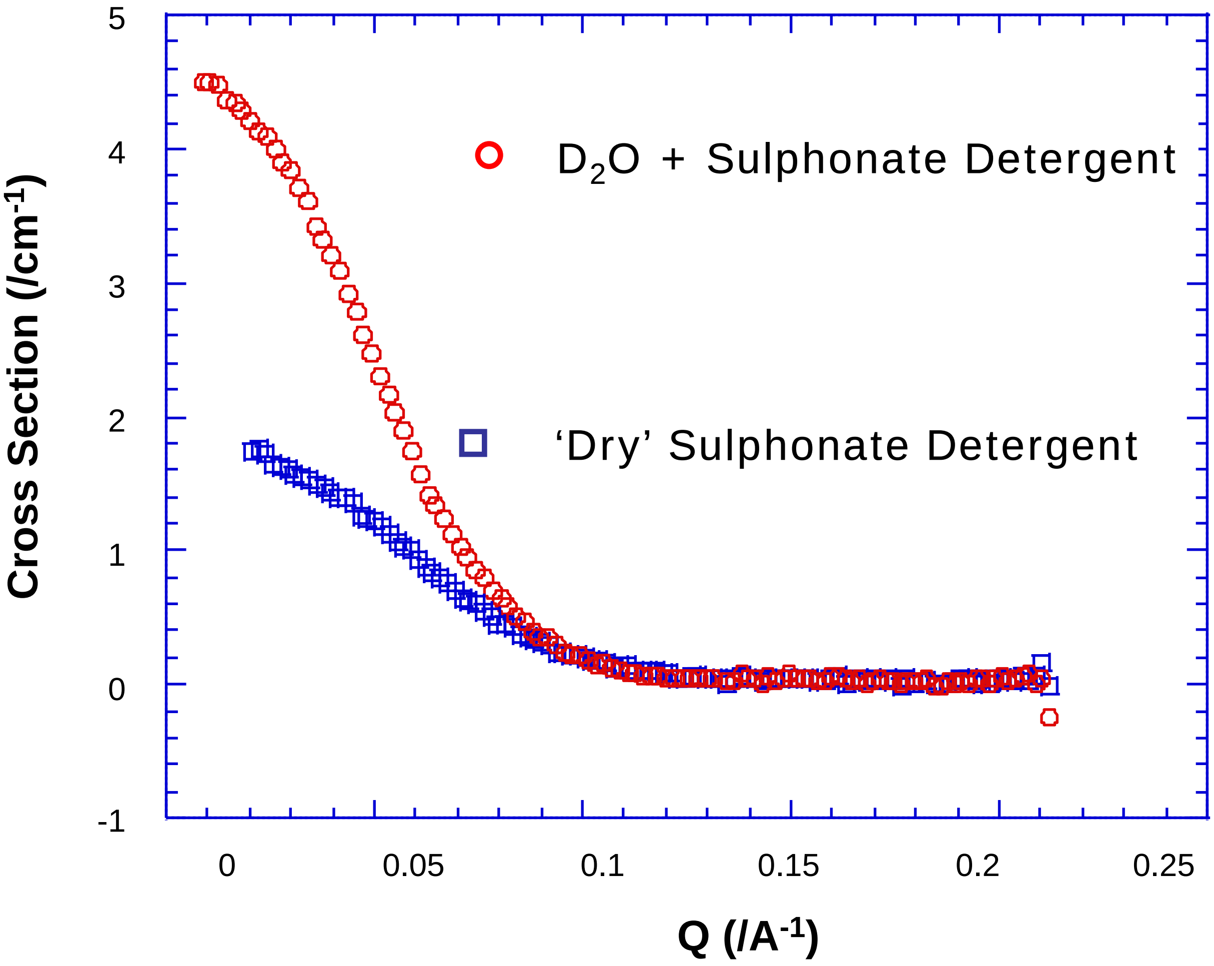
Implies water forming hydrogen bonds/ complexing to sulphonic group.

S=O

Co-ordinated water

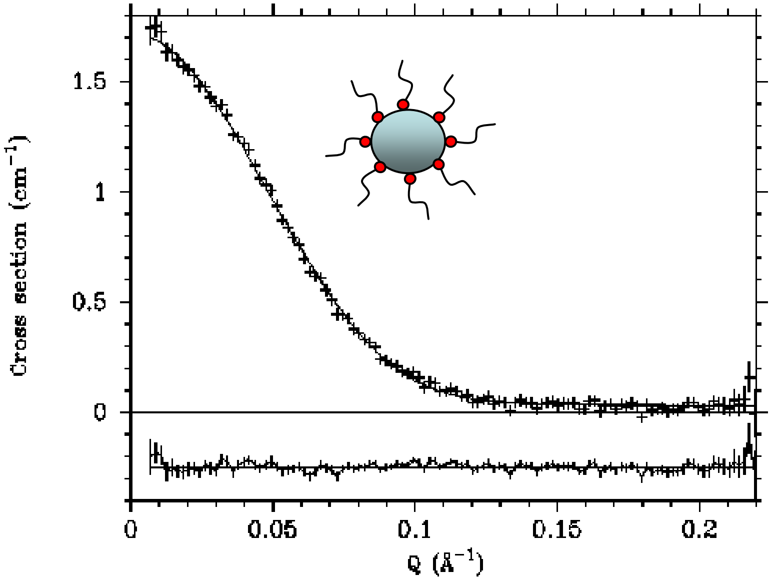
Interaction of Water with Sulphonate Detergents

SANS - Results



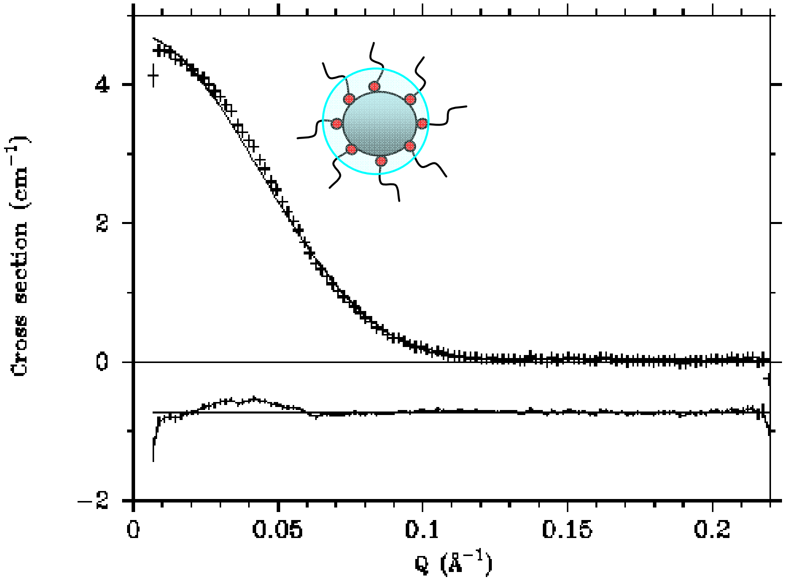
SANS – Fits for Wet and Dry Sulphonate

Dry Sulphonate Detergent



Fitted to hardsphere model.
Core radius 3 nm

Sulphonate with D_2O Layer

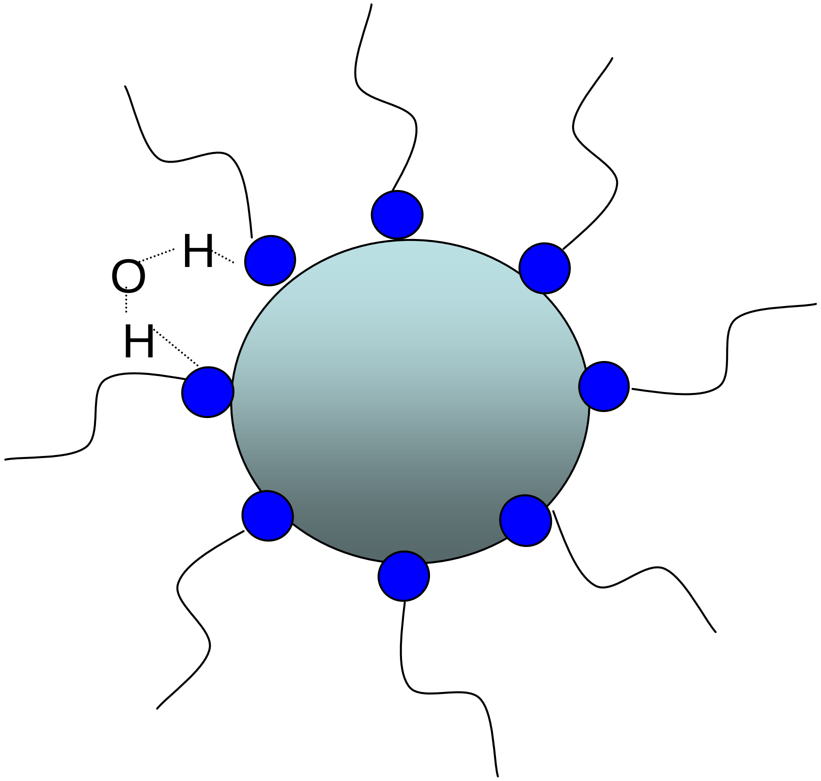


Core shell model, fitted with
Core radius of 3 nm
D_2O layer of 1.8 Å

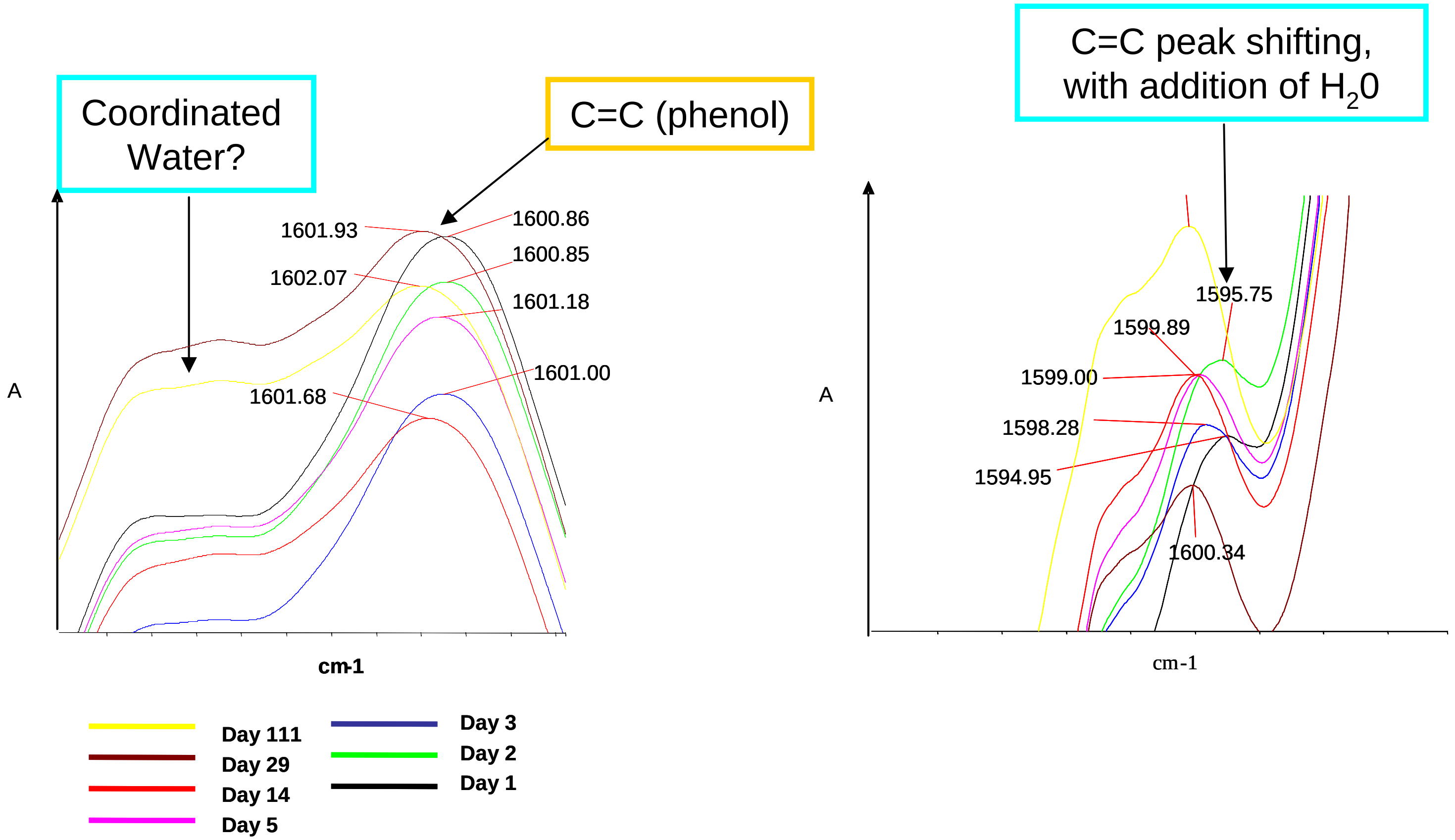
Hypothesis of Water Interaction for Sulphonates

- FTIR:
  - Spectrum indicates hydrogen bonding with SO_3 groups. Microemulsion or on surface

- SANS:
  - Monolayer of water around colloid



FTIR-Spectra of Salicylate in Contact with Water Vapour



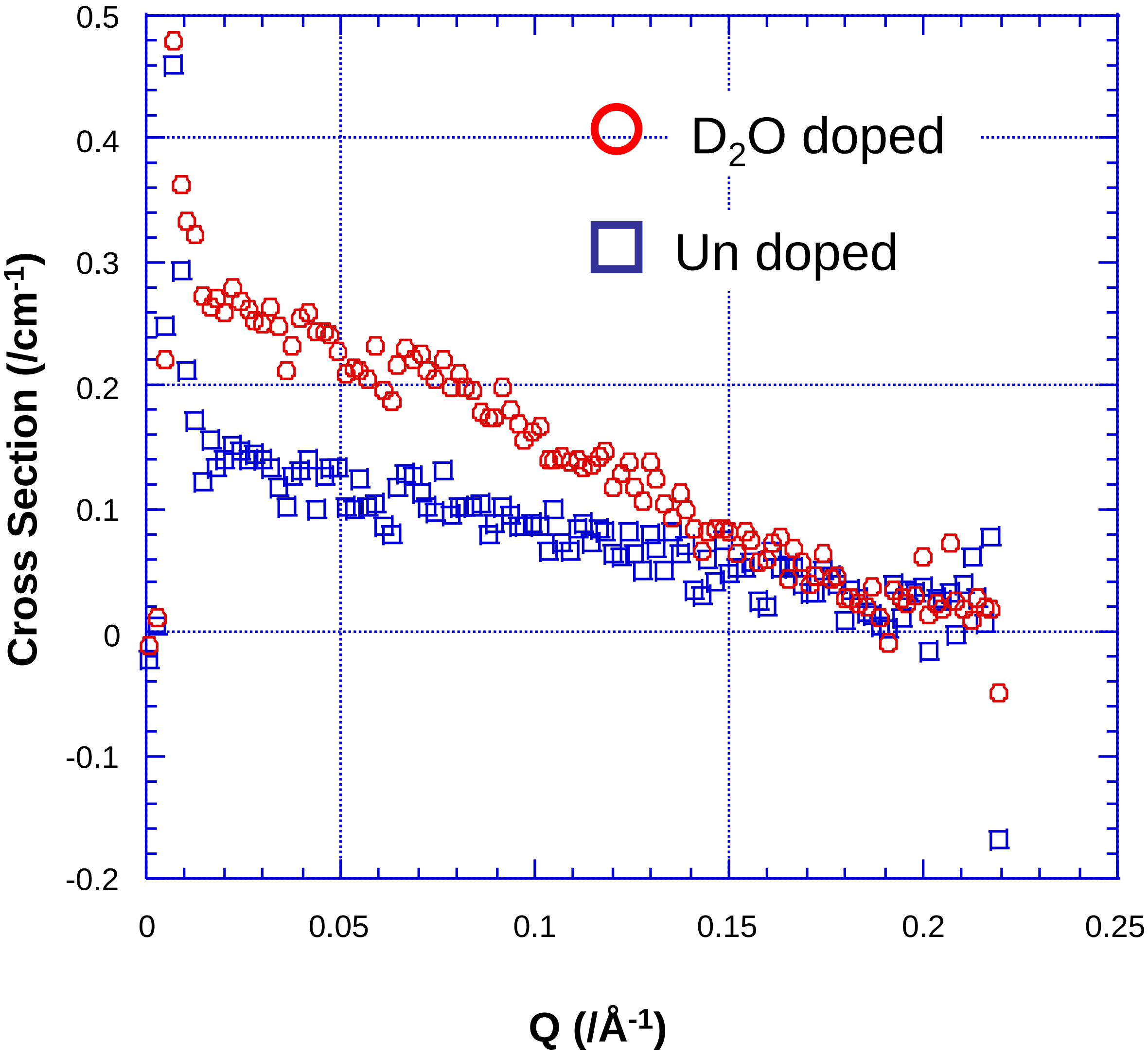
Coordinated Water?

C=C (phenol)

C=C peak shifting, with addition of H_20

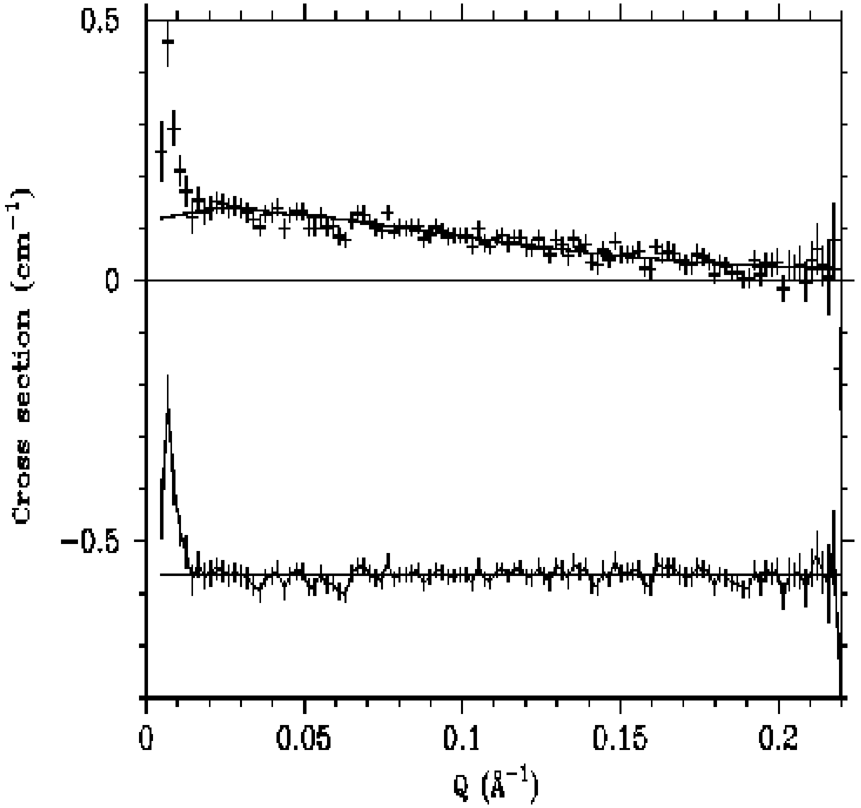
- No intra-molecular bonding seen in surfactants (*i.e.* H bonding) and the absence of C=O peak implies surfactant remains as Ca salt
- Shift of carboxylate and phenol C=C peaks with increasing uptake of water indicate interaction of water with surfactant head group

Interaction of Water with Salicylate Detergents



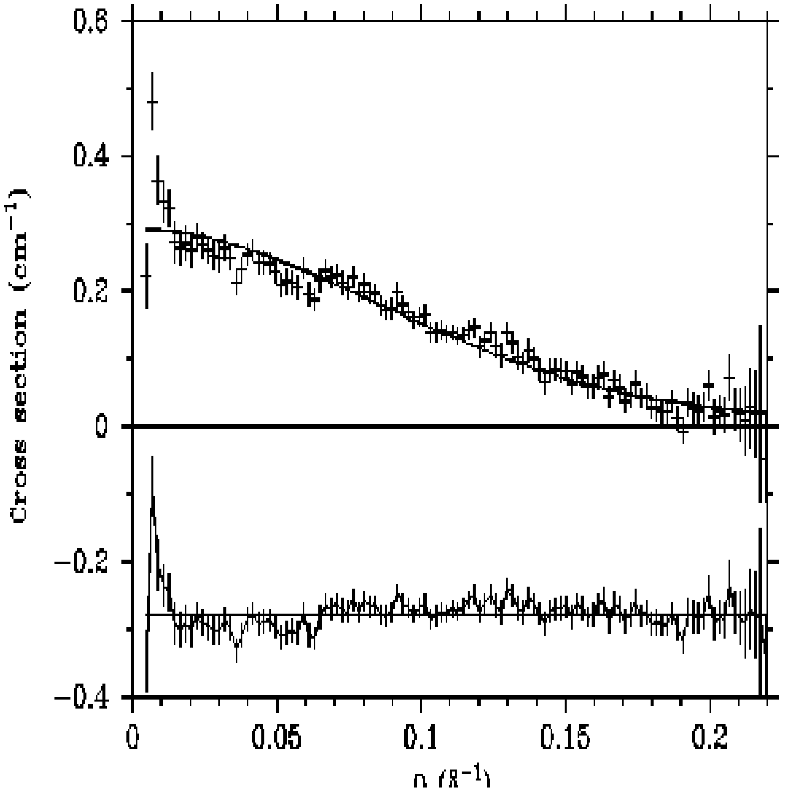
SANS – Fits for Wet and Dry Salicylate

Dry Salicylate Detergent



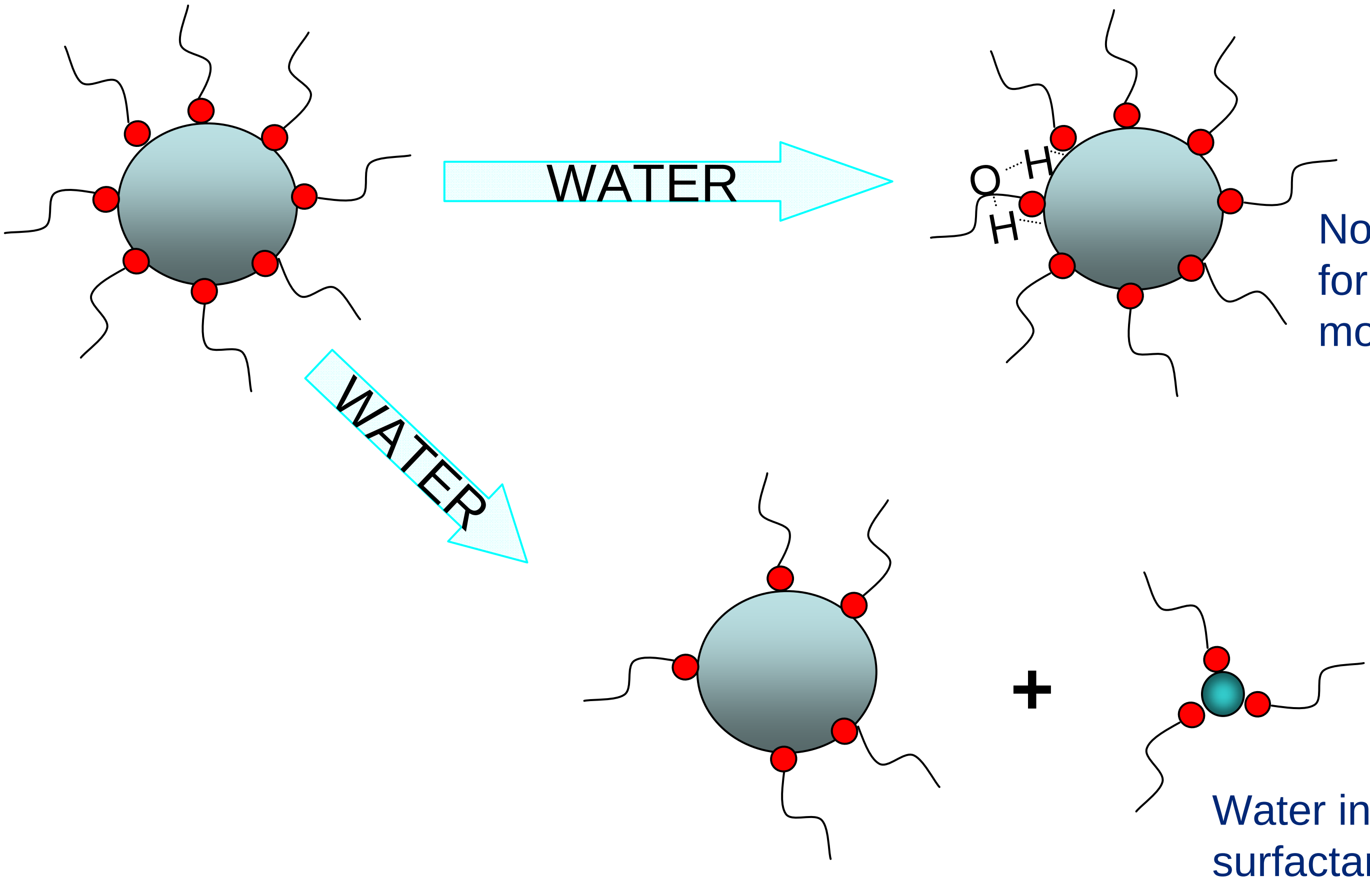
Fitted to hardsphere model.
Core radius 1.4 nm

“Wet” salicylate



Fitted to hardsphere model.
Core radius 0.73 nm

Hypothesis of Water Interaction for Salicylates

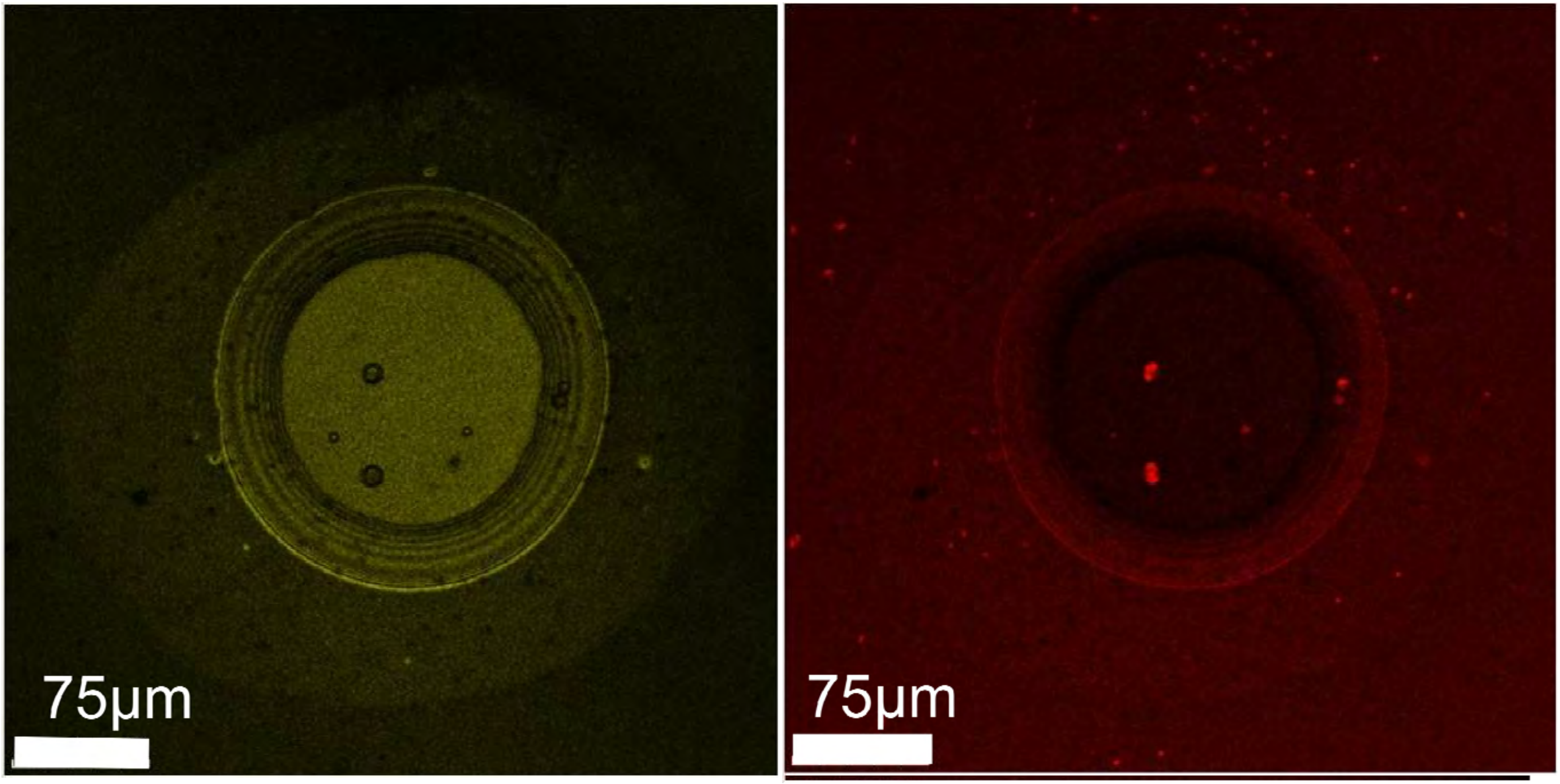


No evidence from SANS for presence of water monolayer

Water interacts with surfactant and strips some surfactant from the particle to form structures

- Salicylate surfactant appears more labile than sulphonate

Confocal Microscopy

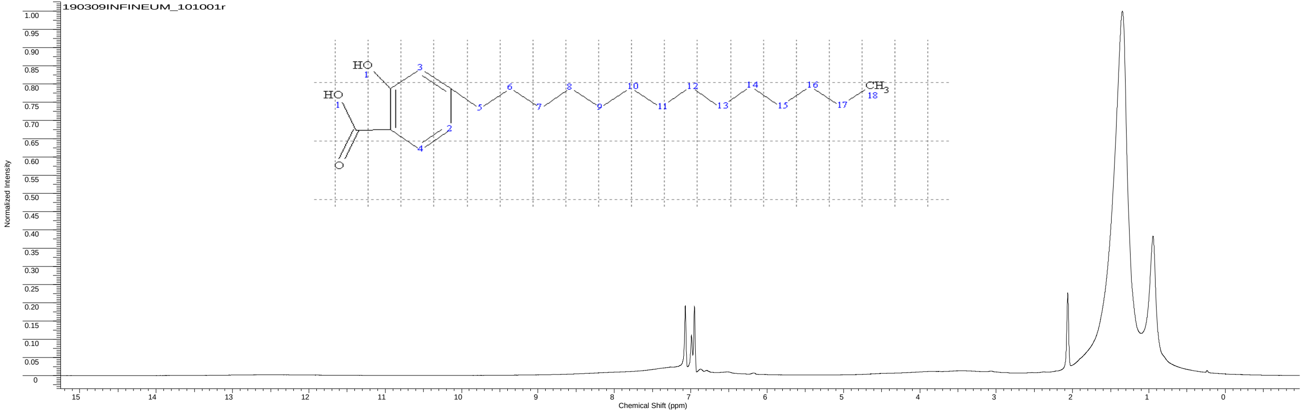


(a) Fluorescein tagged droplets (b) Nile red tagged droplets

- Mixture of 5 wt% salicylic acid, dodecane and water

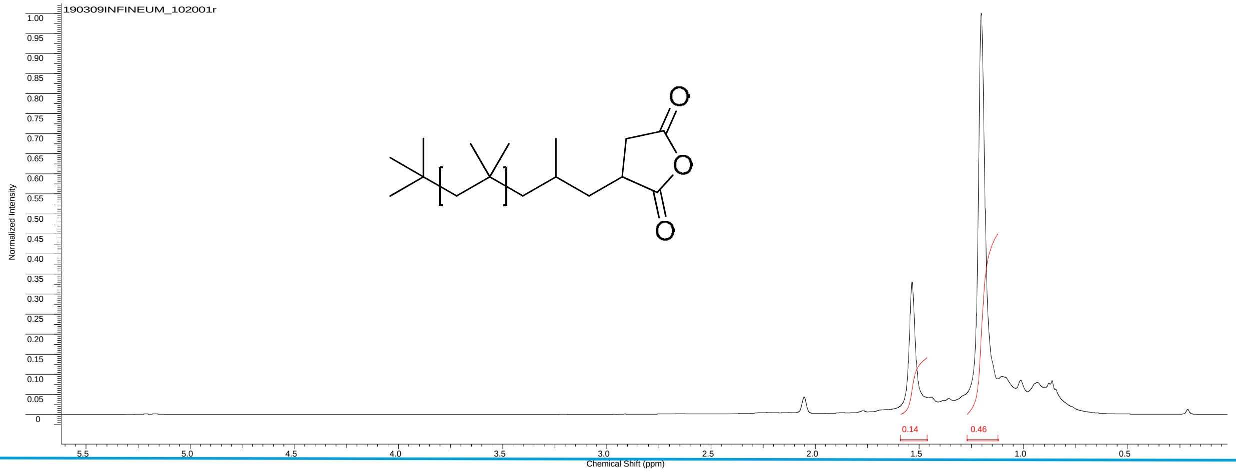
NMR Diffusion Studies of Competitive Adsorption

- Ca Salicylate Particles (r_1 = 14Å)



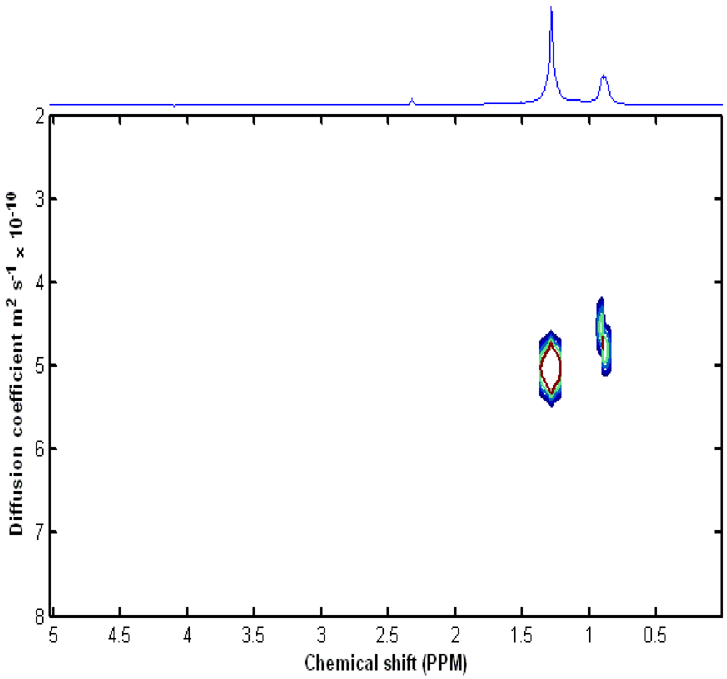
  - Spectra shows minor components that may be from impurities.

- Polyisobutylene Succinic Anhydride (PIBSA)



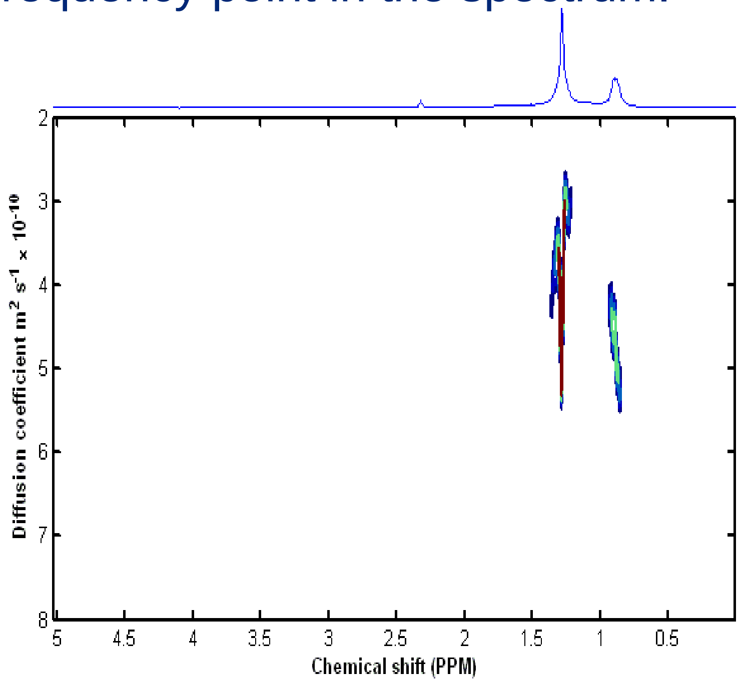
DOSY Plot Type Analysis*:

- Two alternative methods of analysis
- Single peak, one component diffusion analysis.
- Diffusion values calculated for each frequency point in the spectrum.



•The analysis shows two peaks

•Diffusion values lower than multi-component due to single component fit



•Show the same range as the multi-component analysis

•Very complex pattern from the calculation

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* DOSY tool box, Dr. Mathies Nilson from Manchester University

Summary of Individual Systems

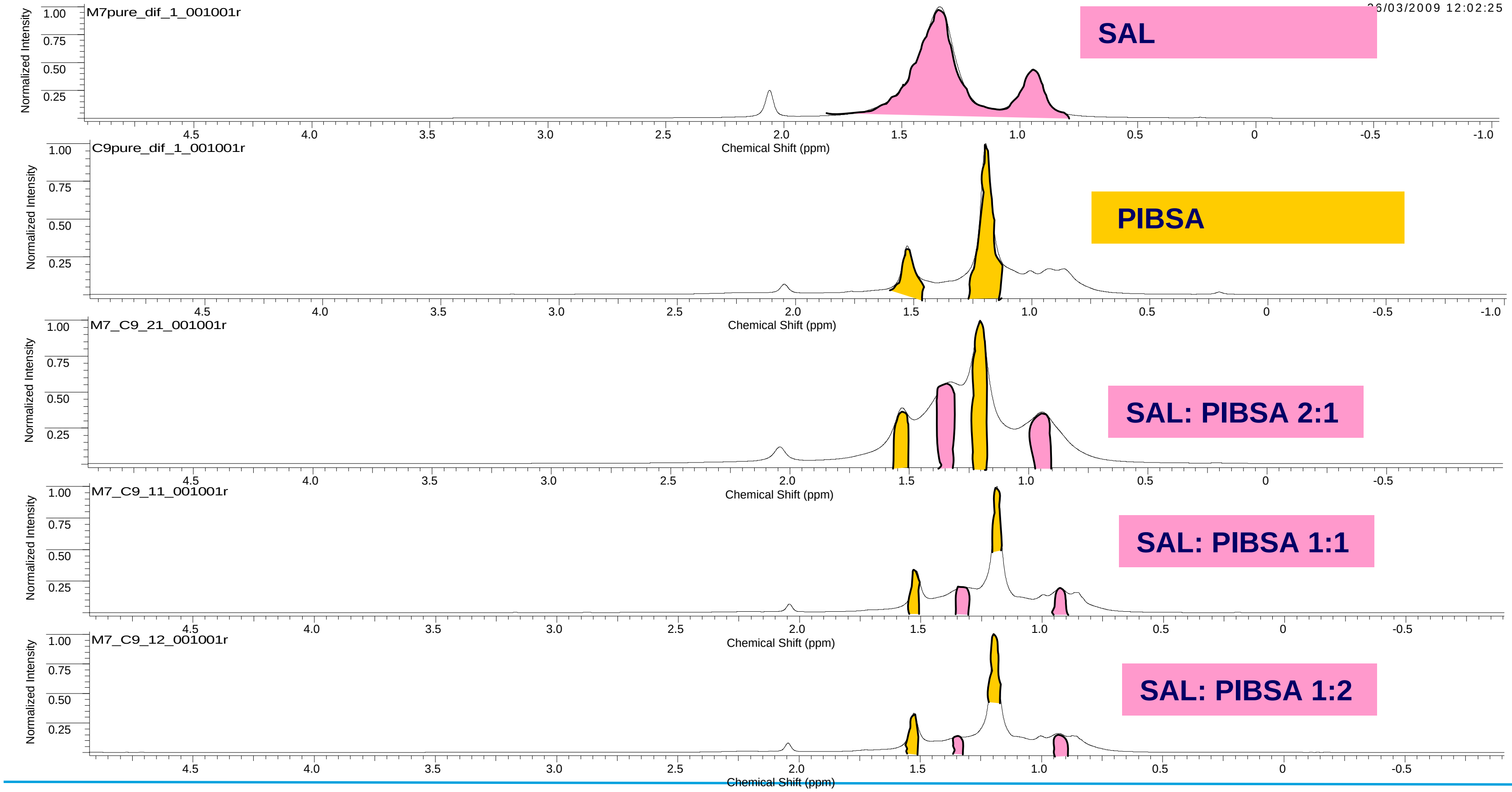
- Salicylate Particles:
  - The single peak analysis for the two peaks of interest gives the same diffusion coefficient of 1.3 x10^{-10} m^2/s,
  - Multi component fit shows two components, one faster than the pure material and one slower.
  - Unbound Surfactant: 3.9x10^{-10} m^2/s, Bound Surfactant: 7.1x10^{-11} m^2/s.

- PIBSA:
  - The two signals of interest have similar diffusion values of 2.4 and 2.6 x10^{-10} m^2/s suggest unbound surfactant

- Effect of Concentration:
  - Both samples experience a reduction of diffusion coefficient with increased concentration, possibility due to aggregation
  - In the case of the PIBSA, a two component fit was used
  - The percentage of the faster component decreases as function of concentration, until a constant value of 50%

Mixtures of Salicylate and PIBSA

- The ratio of SAL: PIBSA was varied



SAL

PIBSA

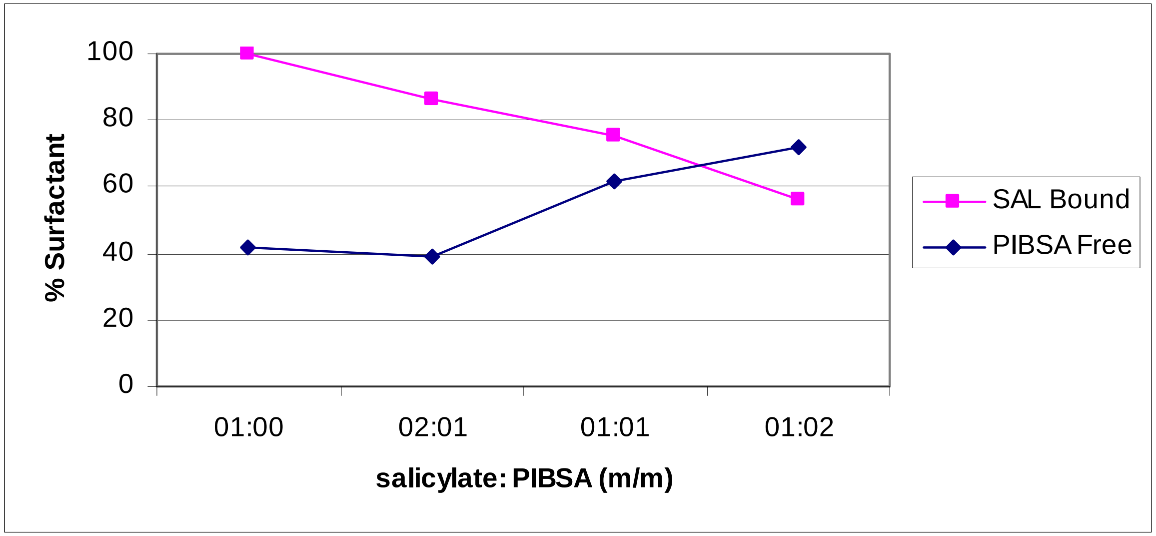
SAL: PIBSA 2:1

SAL: PIBSA 1:1

SAL: PIBSA 1:2

Mixtures of Salicylate and PIBSA

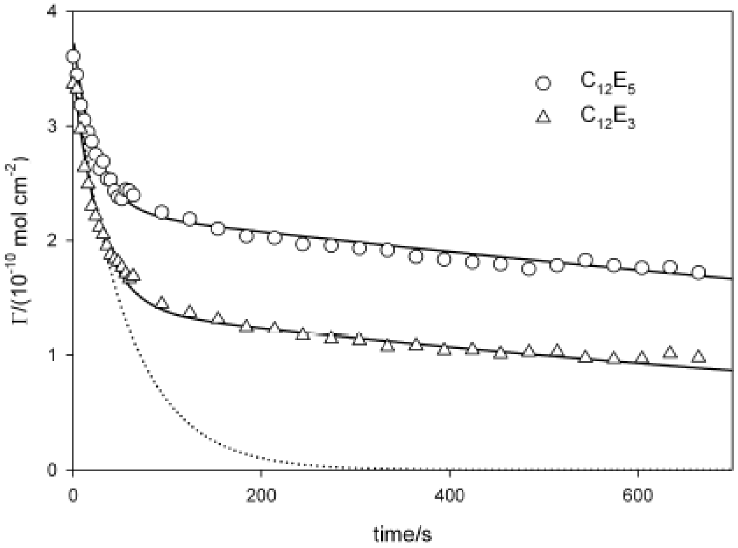
- Analysis of salicylate signal suggests:
    - Increasing [PIBSA] reduces the level of bound salicylate
- Analysis of the PIBSA signal suggests:
    - Two components: one bound (similar to salicylate), one unbound



- Possible mechanism, as [PIBSA] is increased:
    - PIBSA initially displaces salicylate and adsorbs onto the particle
    - At higher concentrations, further salicylate is desorbed without further adsorption of PIBSA: forms a mixed micelle with salicylate?

Effect of Surfactant Structure on Adsorption/ Desorption

- FTIR ATR studies of surfactant adsorbed from toluene onto silica particles
- Studies performed as a function of surfactant head-group size
- Desorption is a two-stage process: initially rapid, followed by a slower desorption
- Larger head group results in slower desorption



Conclusions

- Overbased detergents are used in lubricant additive packages to ensure piston cleanliness and to neutralise acids
- Detergents are surfactant stabilised inorganic particles which can be produced on a multi-tonne scale with consistent size/ size distribution
- For acids dispersed in large droplets, neutralisation occurs via a consumption mechanism
- Water interacts with sulphonate detergents to form a monolayer around the detergent core
- Water interacts with salicylate detergents to desorb a proportion of the more labile salicylate surfactant
- Salicylate surfactant undergoes relatively rapid exchange and can be displaced from the particle surface

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