



## Competition at the nanoparticle surface: a subtle tale of antagonism and cooperation

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### Multi-component stabilisation

Multi-component stabilisation systems widely used.  
Cooperation between a mixture of surfactants and polymers is what is desired.

- when does this offer improved stabilisation?
- when do interactions between polymer and surfactant reduce stability?

Incentives towards multi-component systems:

- reduced shipping weight → transport costs, reduced CO<sub>2</sub> emissions
- reduced material consumption → less water pollution



### Multi-component stabilisation

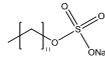
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- Anionic silica – 15nm diameter



- Sodium dodecyl sulfate  
- anionic surfactant (SDS)

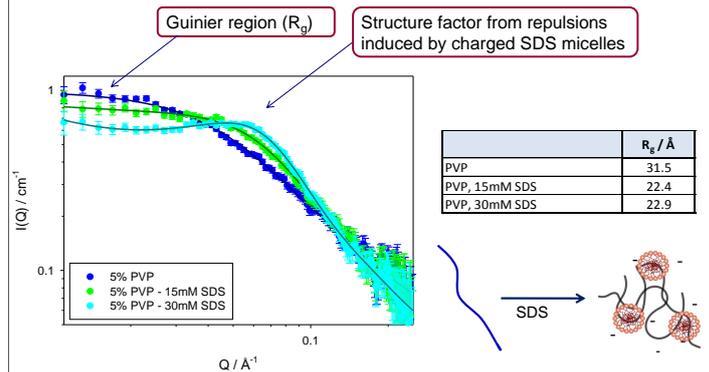


- Poly(vinyl pyrrolidone) - PVP  
- 40K non-ionic polymer

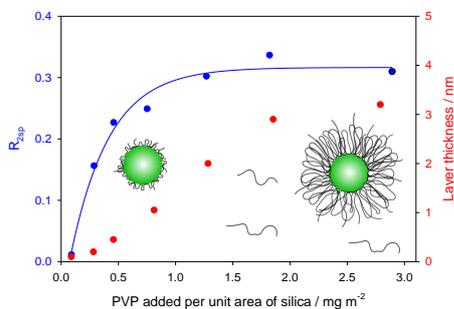


### SANS on PVP + SDS

SDS and solvent contrast matched – all scattering is from PVP

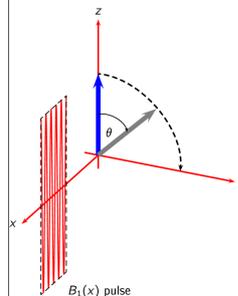


### Adsorption of PVP onto silica



### Relaxation NMR

Direct measurement of concentrated dispersion



Rate for spin system to return to equilibrium:

- longitudinal relaxation ( $R_1$ )
- transverse relaxation ( $R_2$ )

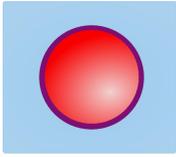
Influenced by

- local magnetic environment
- nuclei present
- correlation times (molecular motions)

Typical rates for solvent relaxation:

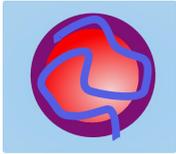
- water: 0.45 s<sup>-1</sup>
- SiO<sub>2</sub>: 3 s<sup>-1</sup> (dispersion)
- glycerol: 20 s<sup>-1</sup>
- CuSO<sub>4</sub>: 100 s<sup>-1</sup> (10 mM)

### Relaxation NMR



- Relaxation of near-surface water much faster than bulk water
- Fast-exchange limit
- Population-average measured:

$$R_{\text{average}} = \phi_{\text{surface}} R_{\text{surface}} + (1 - \phi_{\text{surface}}) R_{\text{bulk}}$$



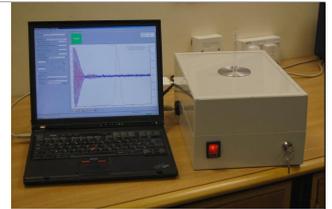
- Adsorbed polymer increases average rate of relaxation
- Molecular motions restricted
  - correlation times longer
  - relaxation more efficient
- More molecules in near-surface layer ( $\phi_{\text{surface}}$  increases)

### New NMR hardware

- Small, light, low power
- Fast measurements
- Low capital costs
- Low running costs

Measure relaxation

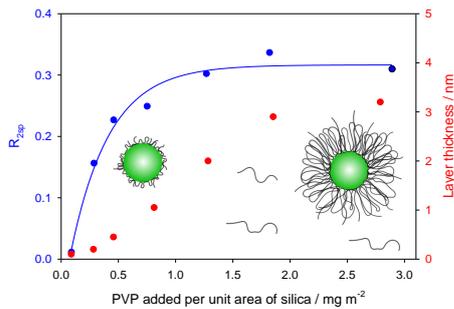
- $R_1$  and  $R_2$
- surface area
- surface chemistry
- flocculation



acorn area™



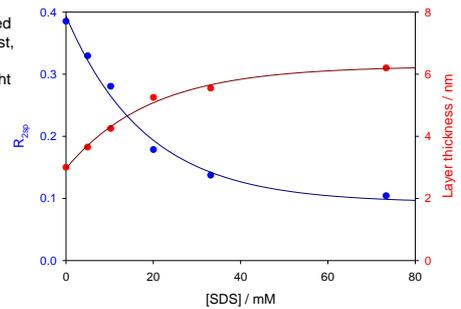
### Polymer adsorption



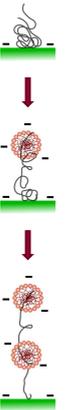
Relaxation NMR sensitive to polymer trains but not to loops

### Desorption by surfactant

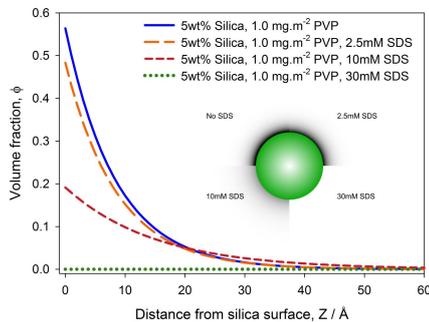
PVP adsorbed onto silica first, SDS added after overnight mixing.



- SDS does not adsorb onto silica ( $R_{2sp}$  bare silica + SDS = 0)
- Decrease in  $R_{2sp}$  suggests less PVP at the silica interface
- Increase in layer thickness → stretching of remaining PVP

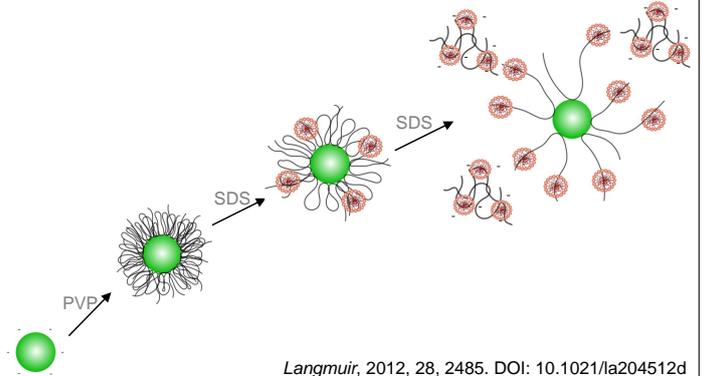


### Polymer volume fraction profile: SANS



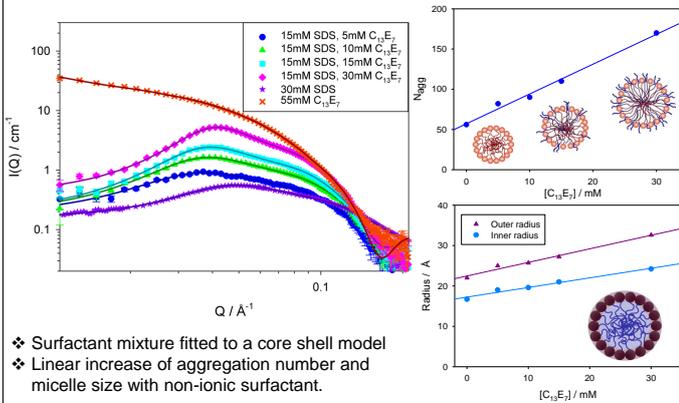
- scattering only from adsorbed polymer
- diffuse layer model → segment profile
- volume fraction profile constrained to other measurements
- layer becomes more elongated and more diffuse with SDS addition

### Polymer desorption by anionic surfactant



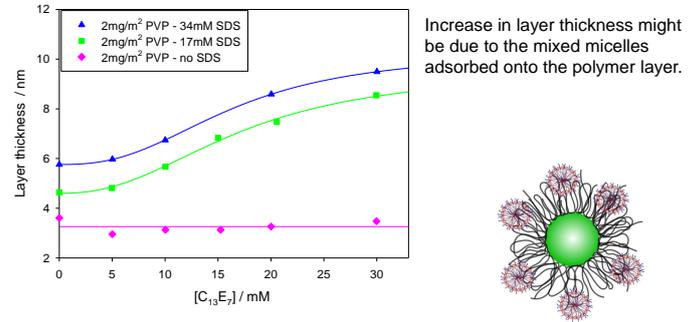
Langmuir, 2012, 28, 2485. DOI: 10.1021/la204512d

### Surfactants mixture: SDS + C<sub>13</sub>E<sub>7</sub>

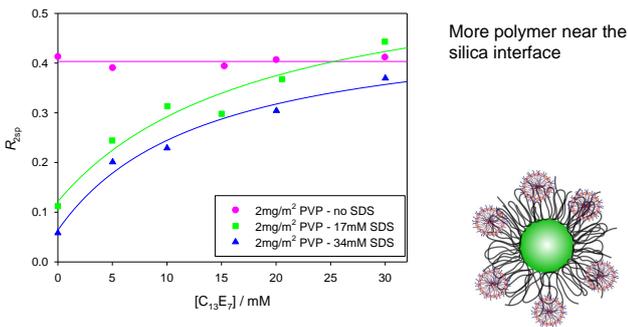


- Surfactant mixture fitted to a core shell model
- Linear increase of aggregation number and micelle size with non-ionic surfactant.

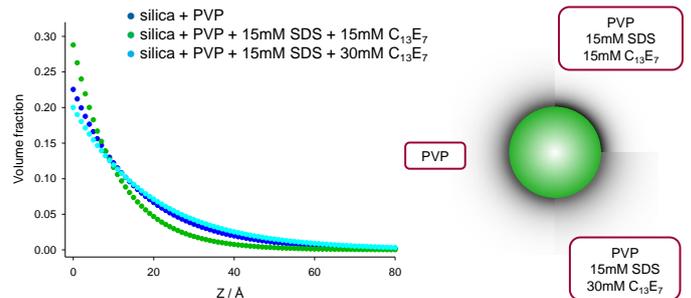
### Adsorbed layer: C<sub>13</sub>E<sub>7</sub>+SDS+PVP+silica



### Near-surface polymer: C<sub>13</sub>E<sub>7</sub>+SDS+PVP+silica



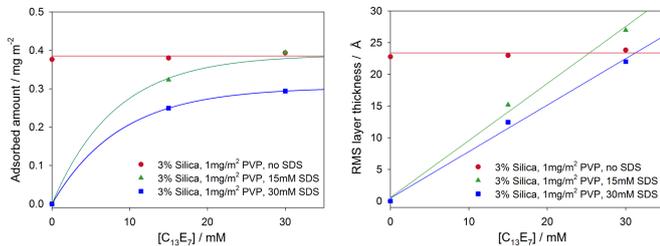
### Polymer volume fraction profile from SANS



- C<sub>13</sub>E<sub>7</sub> displaces SDS from micelles reducing repulsion
- adsorbed amount increases with addition of C<sub>13</sub>E<sub>7</sub>

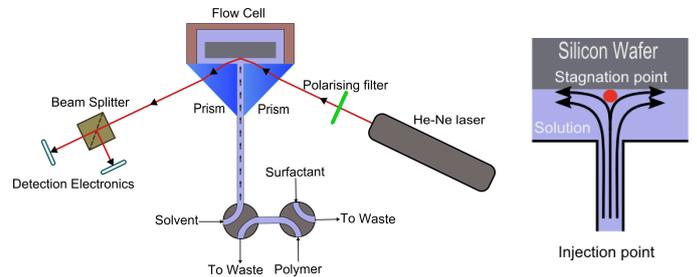
### Adsorption/desorption summary from SANS

Data extracted from fittings from the Diffuse Layer Model



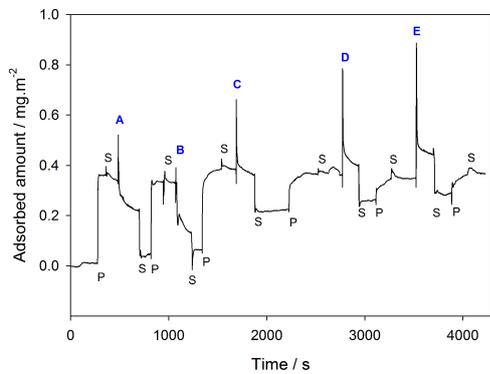
- Support solvent relaxation NMR and light scattering results.
- Addition of non-ionic surfactant to the silica, PVP, SDS system
  - increases the amount of polymer at the silica interface
  - extends the polymer layer adsorbed at the interface

### Fixed-angle optical reflectometry

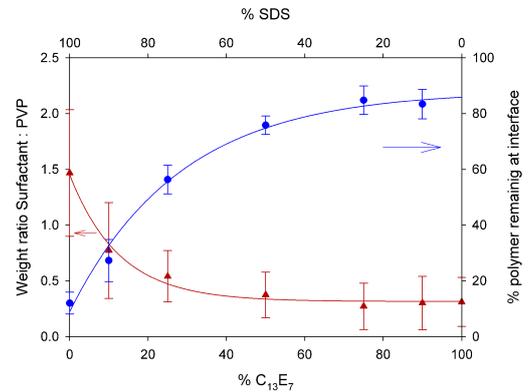


refractive index changes → polymer adsorbed amount changes

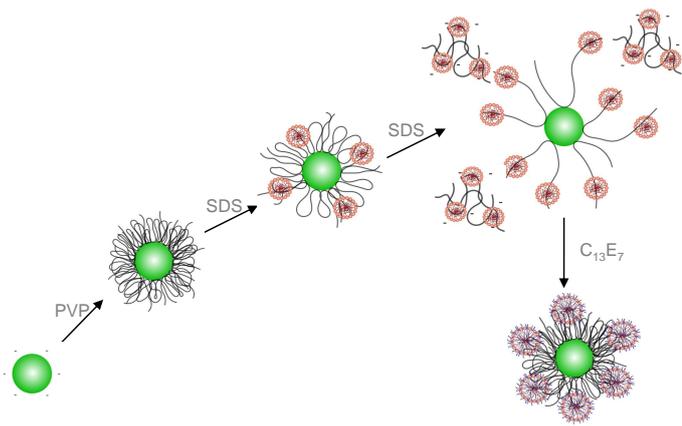
### Sample reflectometry data



### Surfactant-mediated desorption



### Polymers and surfactants at the interface



Langmuir, 2012, 28, 6282. DOI: 10.1021/la300282m

### Conclusions

- SDS complexes with PVP and leads to:
  - some desorption of polymer
  - elongation of remaining polymer chains
  - a more diffuse adsorbed layer
- Addition of  $C_{13}E_7$  leads to
  - no effect in absence of SDS
  - competition with SDS in adsorbing micelles
  - reduction in repulsion within layer
- Adsorbed polymers are more labile than you may think
- NMR is a great tool for chasing after molecules

Langmuir, 2012, 28, 2485. DOI: 10.1021/la204512d  
Langmuir, 2012, 28, 6282. DOI: 10.1021/la300282m

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- Martien Cohen Stuart (Wageningen)

