Molecules at the solid-liquid interface: a miniature NMR to characterise colloidal systems

Beatrice Cattoz, Catherine L. Cooper,
Stuart W. Prescott, Terence Cosgrove

School of Chemistry
University of Bristol

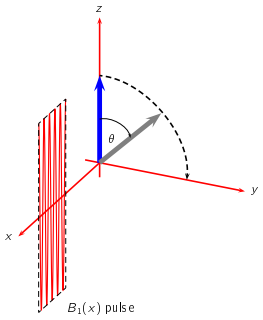
stuart.prescott@bristol.ac.uk

Outline

1. What is relaxation NMR?
2. Miniaturised NMR
3. Polymers at surfaces
   - In what conformations do polymers adsorb?
   - Do we see synergistic or antagonistic effects between polymers and surfactants?
   - What are the early indications of colloidal instability?

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

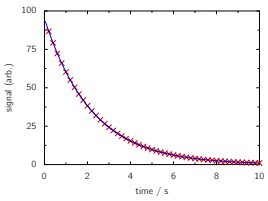
- local magnetic environment
- nuclei present
- correlation times (molecular motions)

Measurement takes

- R_1: inversion recovery, $\sim$ 5 min
- R_2: CPMG, $\sim$ 30 s

Relaxation rates

Multi-pulse pulse sequence gives decay of signal with time



$$\Downarrow$$

$$R_2 = 0.5\,\mathrm{s}^{-1}$$

Measurements

- frequency-resolved rates (*e.g.* relaxation of peak at $\delta \sim$1.5ppm)
- average rate (*i.e.* solvent)

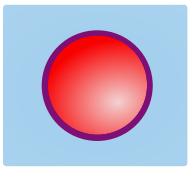
Typical rates for solvent relaxation:

water	$0.45\,\mathrm{s}^{-1}$
SiO_2	$3\,\mathrm{s}^{-1}$ (dispersion)
glycerol	$20\,\mathrm{s}^{-1}$
$CuSO_4$	$100\,\mathrm{s}^{-1}$ (10 mM)

Two limits for behaviour

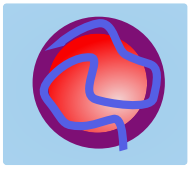
- fast exchange (one average rate)
- slow exchange (two rates)

Solvent relaxation



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

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

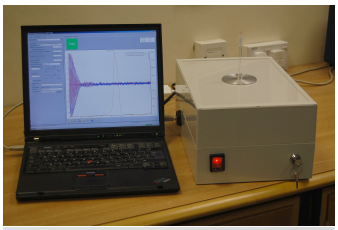


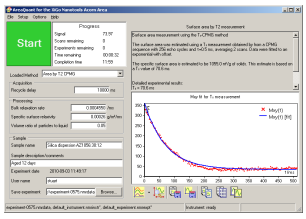
- Adsorbed polymer increases average rate of relaxation
- Molecular motions restricted
  $\Rightarrow$ correlation times longer
  $\Rightarrow$ relaxation more efficient
- More molecules in near-surface layer (ϕ_{surface} increases)

Miniature 13 MHz NMR

Requirements:

- Small, portable
- Low power (< 50 W)
- USB connection
- Doesn't need an NMR expert





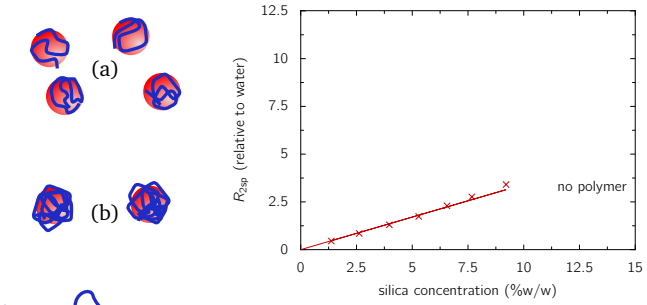
Assumptions for a miniature NMR

Low resolution
- No chemical shift resolution
- Fine tuning not important
- Only see solvent/continuous phase

Solvent relaxation
- Measurement not very sensitive to tuning
- Don't need to retune for each sample

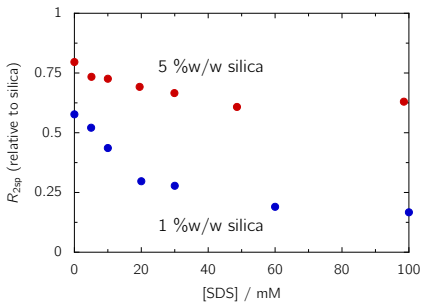
Simple data processing
- time-domain processing
- noise filtering on FID (convolution)
- correct phasing not required
- frequency-domain processing mostly avoided
- auto-tuning using FFT
- magnet setup (manufacture)

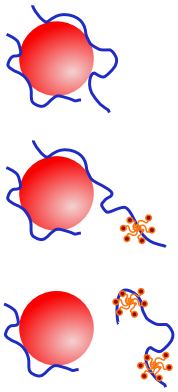
Measuring polymer coverage on nanoparticles



poly(vinyl pyrrolidone) (700k) + SiO_2 (diameter 15 nm)

Polymer-surfactant complexation



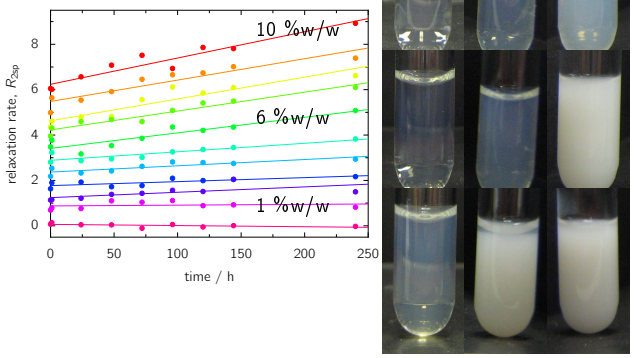


poly(vinyl pyrrolidone) (55k, 2 mg m^{-2} added) + SiO_2 (diameter 15 nm)

DLS & SANS ⇒ see poster P2.19, Beatrice Cattoz

Interactions between poly(styrene sulfonate) and silica

PSSNa (70k) 5%w/w + SiO_2 (15nm diameter)



Conclusions

Polymers at surfaces
- Polymer conformation independent of polymer concentration below "full" coverage
- Antagonistic interactions evident, surfactant complexation and desorption
- Early indication of colloidal instability, depletion flocculation

Solvent relaxation NMR
- pseudo-isotherm, surface area, surface chemistry

⇒ see also:
1. "Targeting non-steroidal drug using polymer encapsulation" Shirin Alexander P2.30
2. "Determination of pore space of a highly monodisperse o/w emulsion using NMR diffusometry" Panithi Wiroonpochit P2.11
3. "PDMS/polyhedral oligomeric silsesquioxane composites" Sairoong Muangpil P5.52

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