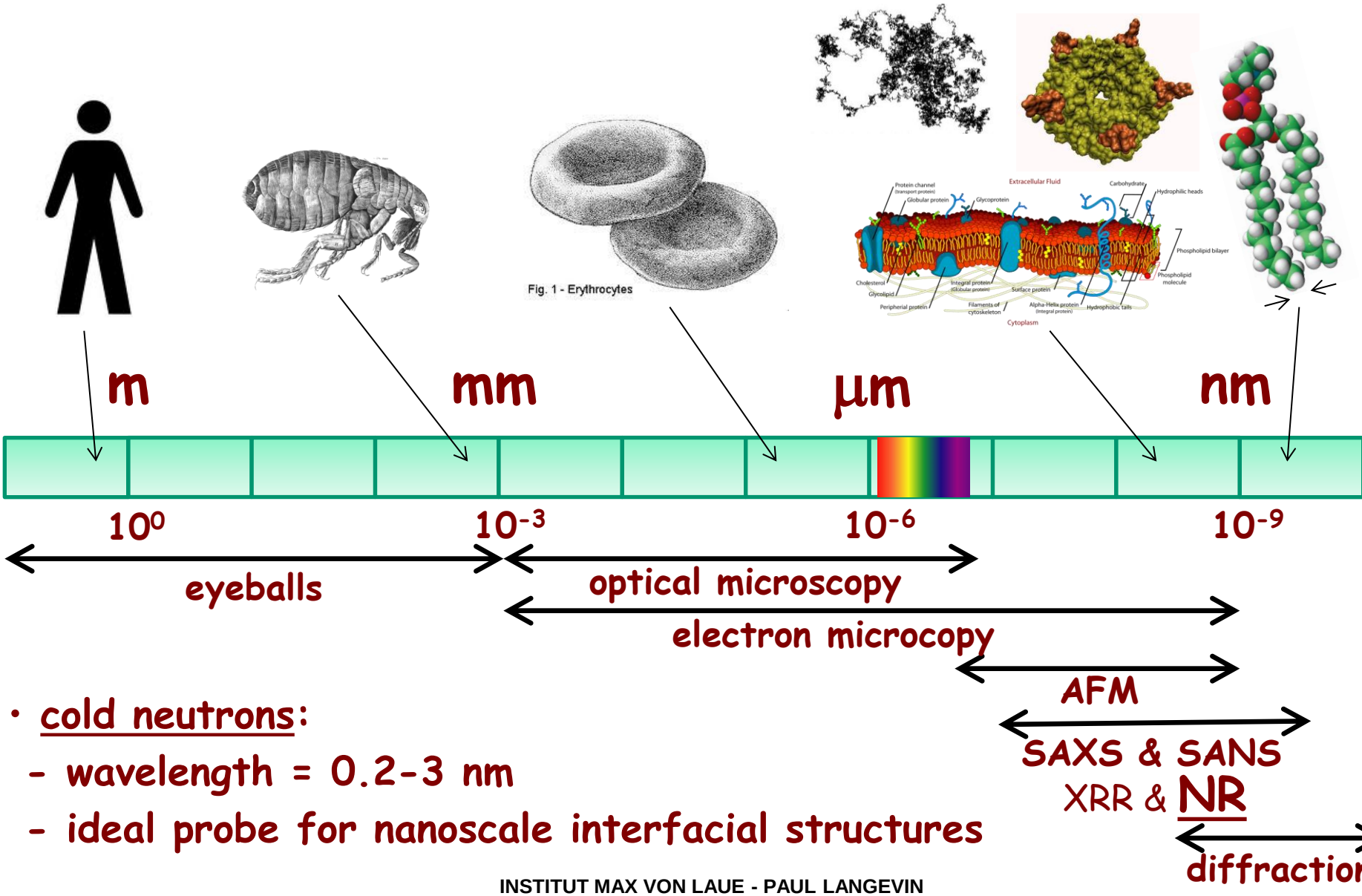
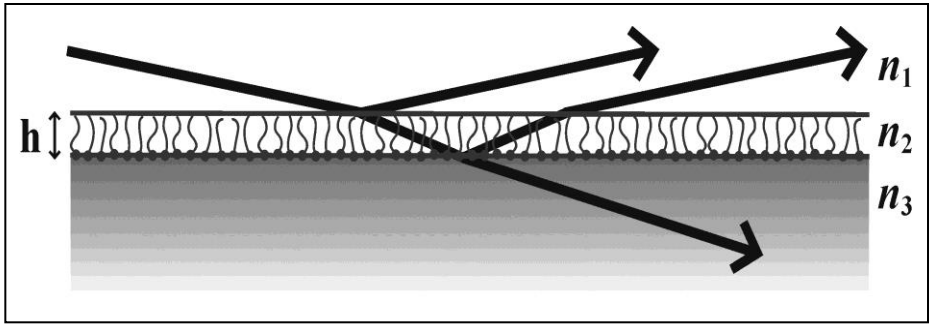
wavelengths for nanoscale interfacial analysis



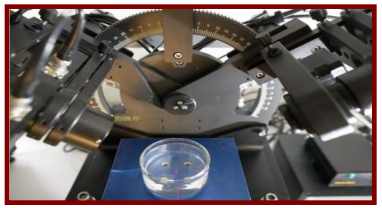
- cold neutrons:
  - wavelength = 0.2-3 nm
  - ideal probe for nanoscale interfacial structures

techniques for nanoscale interfacial analysis

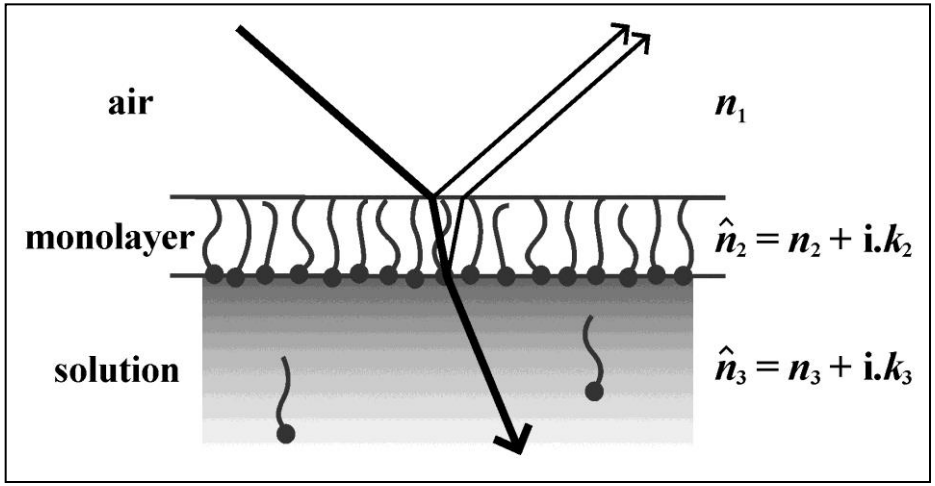
- **neutron reflectometry**:
  - contrast from isotopic labelling
  - specular → structure & composition
  - off-specular → lateral morphology



- **ellipsometry**:
  - precision, sensitivity & fast kinetics
  - calibration to real physical parameters



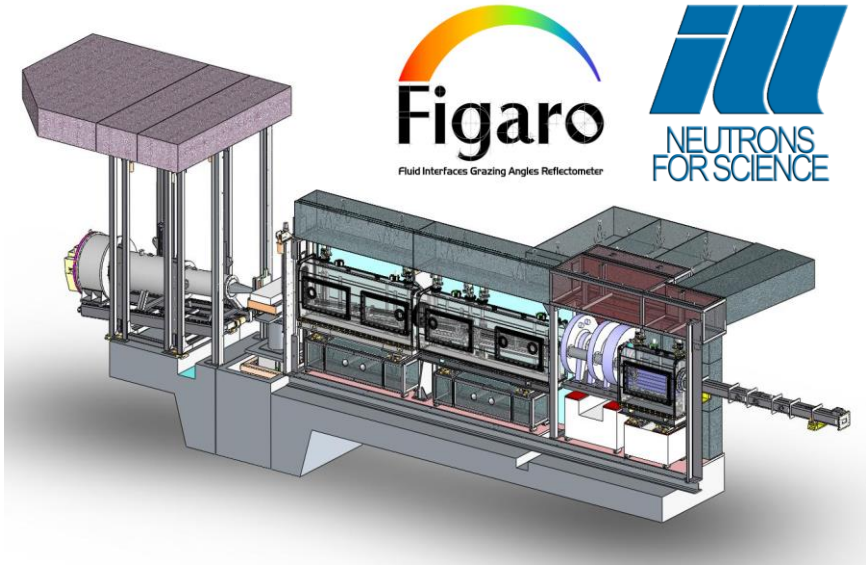
Nucleus	ρ_s / 10^{-5} Å
^{1}H	−3.7406
^{2}H	6.671
C	6.6460
N	9.36
O	5.803



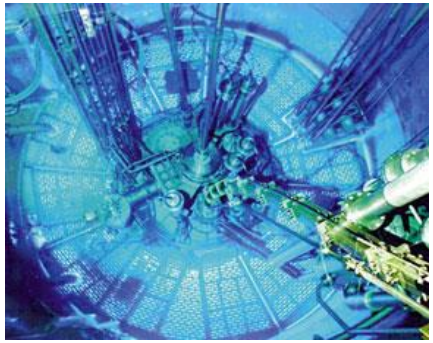
- **other techniques**:
  - surface tensiometry
  - Brewster angle microscopy
  - infrared reflectometry *etc.*

fluid interfaces grazing angles reflectometer

- figaro stats:
  - world-leading instrument from 2009
  - flux at sample: 4 x 10^2 n mm^{-2} s^{-1}
  - large beam size: 0.5-5 mm x 40 mm
  - flexible resolution: 1-10% dq/q
  - dozens of publications: www.ill.eu



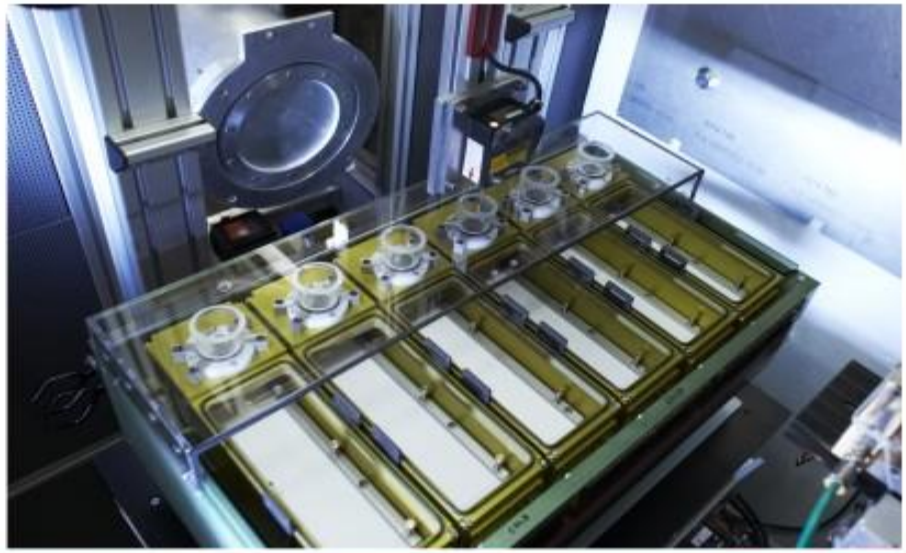
ILL's powerful & stable reactor

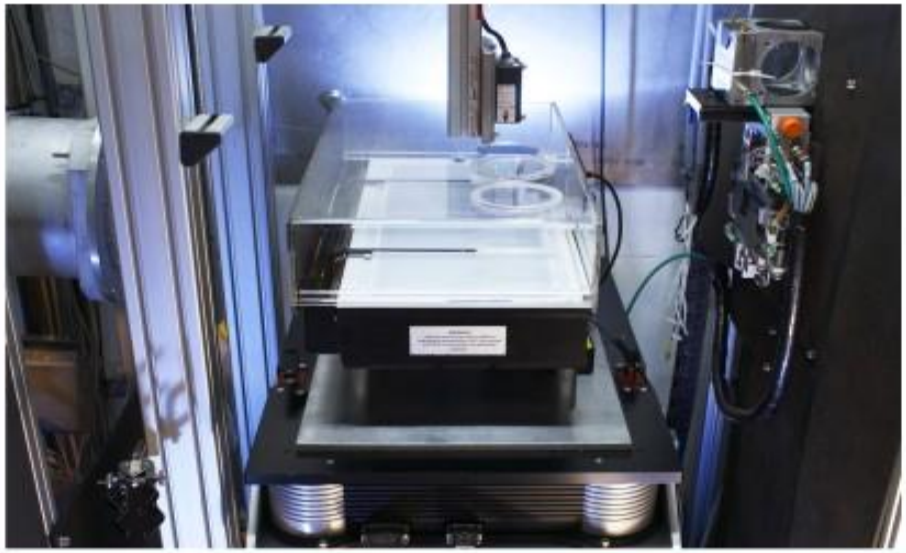


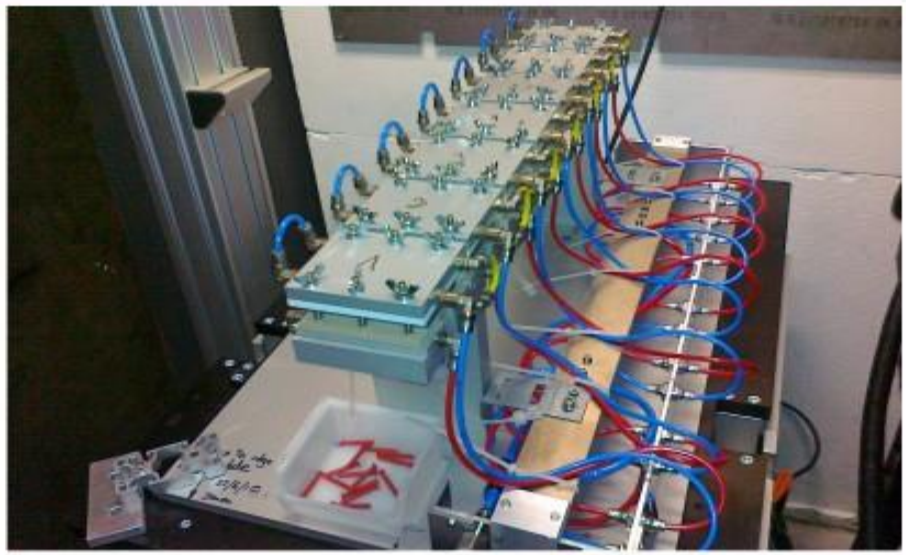
beautifully set in Grenoble

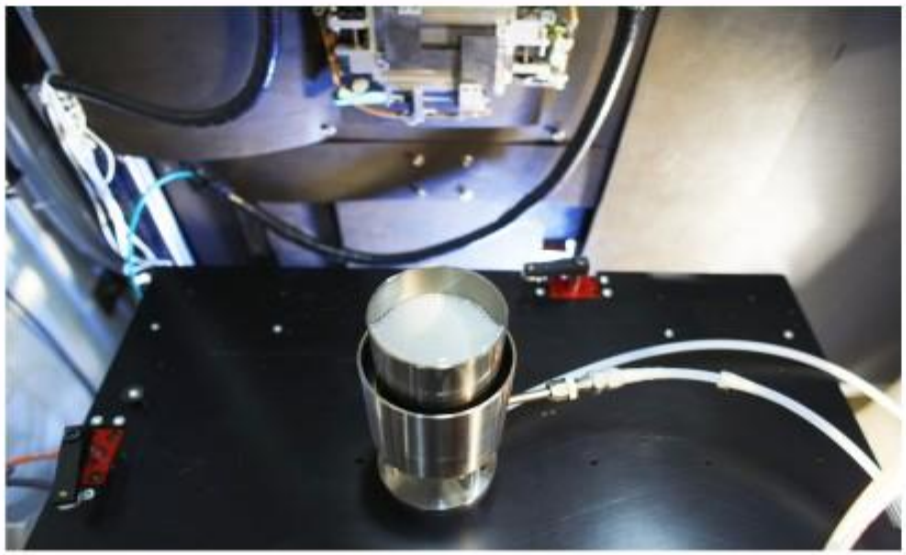
- figaro examples:
  - polymer film structure
  - nanoparticle interactions
  - dna & protein studies
  - solvent drying in glues & paints
  - rheology of polymer blends
  - detergency & formulation mechanisms

figaro sample environments

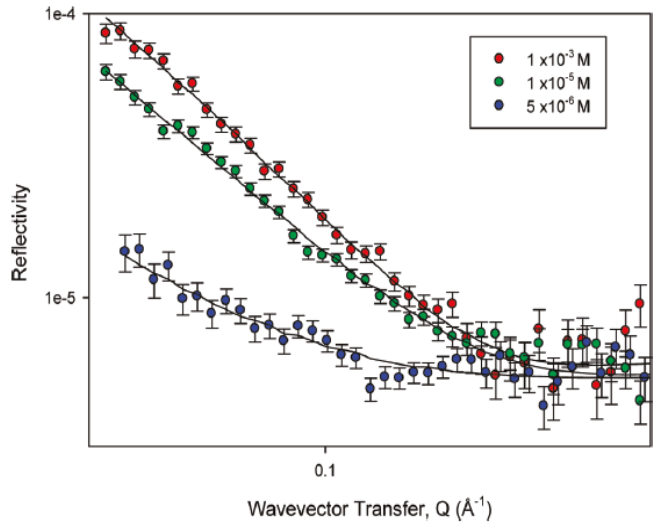


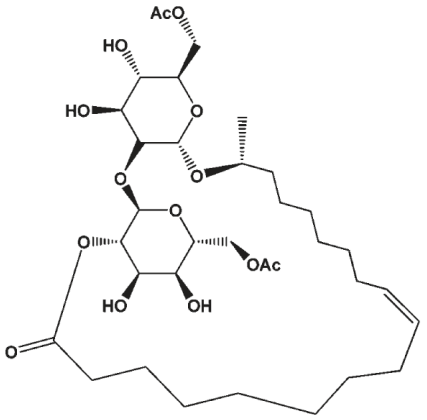


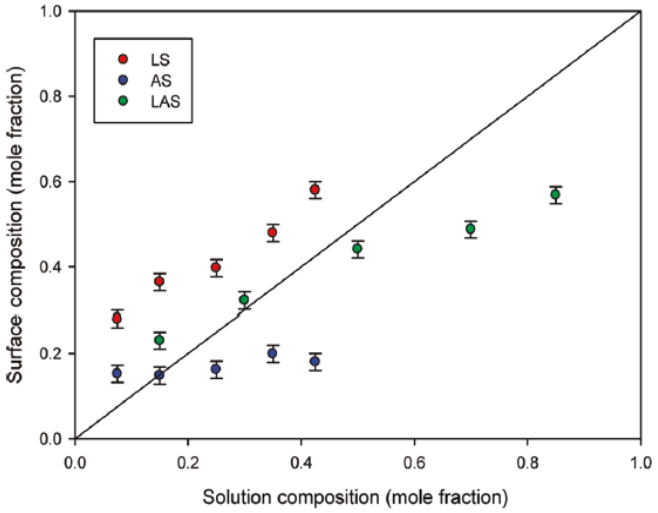


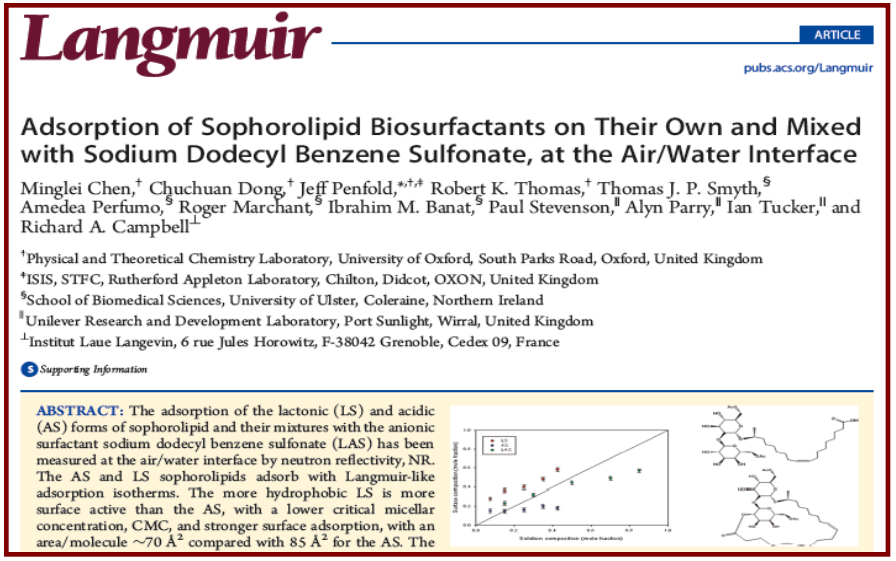


example of air/liquid interface science on figaro









Langmuir ARTICLE

pubs.acs.org/Langmuir

Adsorption of Sophorolipid Biosurfactants on Their Own and Mixed with Sodium Dodecyl Benzene Sulfonate, at the Air/Water Interface

Minglei Chen,[†] Chuchuan Dong,[†] Jeff Penfold,[*,†,‡] Robert K. Thomas,[†] Thomas J. P. Smyth,[§] Amedea Perfumo,[§] Roger Marchant,[§] Ibrahim M. Banat,[§] Paul Stevenson,[∥] Alyn Parry,[∥] Ian Tucker,[∥] and Richard A. Campbell[⊥]

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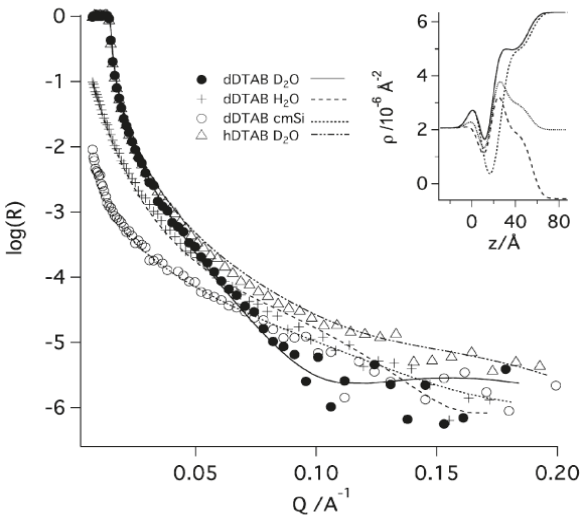
[‡]ISIS, STFC, Rutherford Appleton Laboratory, Chilton, Didcot, OXON, United Kingdom
[§]School of Biomedical Sciences, University of Ulster, Coleraine, Northern Ireland
[∥]Unilever Research and Development Laboratory, Port Sunlight, Wirral, United Kingdom
[⊥]Institut Laue Langevin, 6 rue Jules Horowitz, F-38042 Grenoble, Cedex 09, France

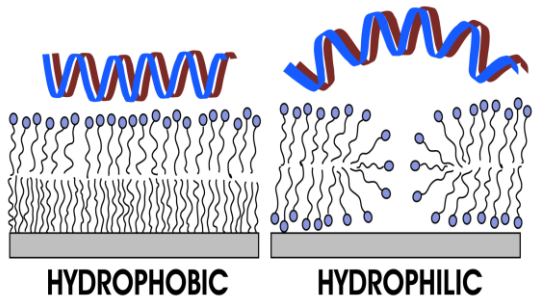
Supporting Information

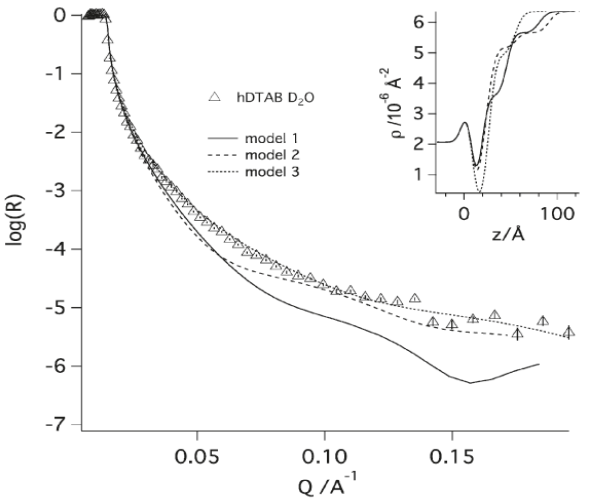
ABSTRACT: The adsorption of the lactonic (LS) and acidic (AS) forms of sophorolipid and their mixtures with the anionic surfactant sodium dodecyl benzene sulfonate (LAS) has been measured at the air/water interface by neutron reflectivity, NR. The AS and LS sophorolipids adsorb with Langmuir-like adsorption isotherms. The more hydrophobic LS is more surface active than the AS, with a lower critical micellar concentration, CMC, and stronger surface adsorption, with an area/molecule ~70 Å^2 compared with 85 Å^2 for the AS. The

- drive to produce surfactants by microorganisms cf. petroleum
- surface composition of three-component mixtures deconvoluted
- biosurfactants dominated surface over conventional surfactants

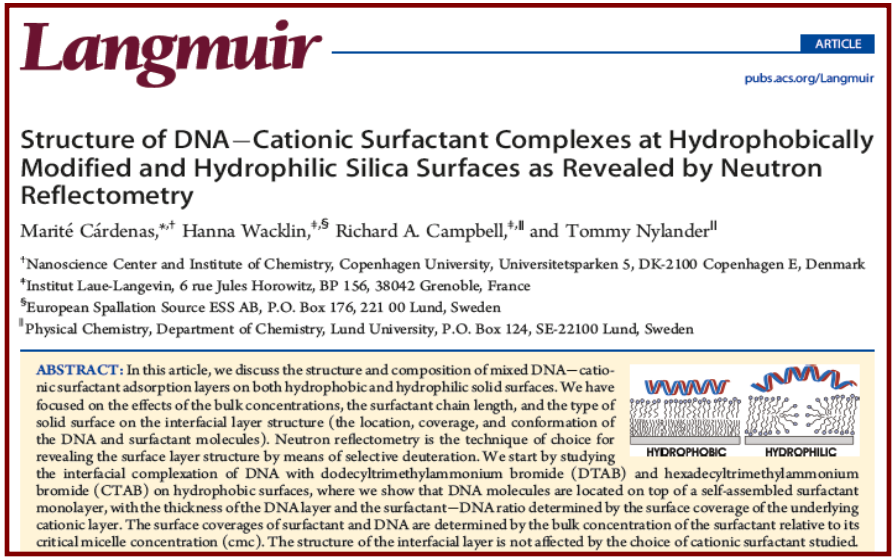
example of solid/liquid interface science on figaro







- study of the interactions of dna with membranes (gene delivery)
- measurements resolved dna structure & surface excess
- dna coverage determined by that of self-assembled surfactant



Langmuir ARTICLE

pubs.acs.org/Langmuir

Structure of DNA—Cationic Surfactant Complexes at Hydrophobically Modified and Hydrophilic Silica Surfaces as Revealed by Neutron Reflectometry

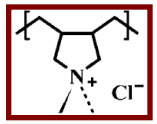
Marité Cárdenas,*,† Hanna Wacklin,‡,§ Richard A. Campbell,‡,∥ and Tommy Nylander∥

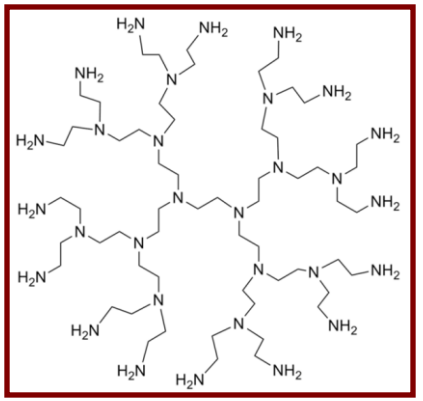
†Nanoscience Center and Institute of Chemistry, Copenhagen University, Universitetsparken 5, DK-2100 Copenhagen E, Denmark
‡Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, France
§European Spallation Source ESS AB, P.O. Box 176, 221 00 Lund, Sweden
∥Physical Chemistry, Department of Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden

ABSTRACT: In this article, we discuss the structure and composition of mixed DNA—cationic surfactant adsorption layers on both hydrophobic and hydrophilic solid surfaces. We have focused on the effects of the bulk concentrations, the surfactant chain length, and the type of solid surface on the interfacial layer structure (the location, coverage, and conformation of the DNA and surfactant molecules). Neutron reflectometry is the technique of choice for revealing the surface layer structure by means of selective deuteration. We start by studying the interfacial complexation of DNA with dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (CTAB) on hydrophobic surfaces, where we show that DNA molecules are located on top of a self-assembled surfactant monolayer, with the thickness of the DNA layer and the surfactant—DNA ratio determined by the surface coverage of the underlying cationic layer. The surface coverages of surfactant and DNA are determined by the bulk concentration of the surfactant relative to its critical micelle concentration (cmc). The structure of the interfacial layer is not affected by the choice of cationic surfactant studied.

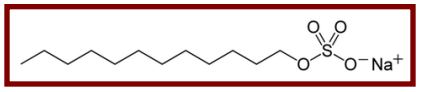
interfacial behavior of complex mixtures

- <u>cationic polyelectrolytes</u>:
  - poly(diallyldimethylammonium chloride) [Pdadmac]
  - poly(ethylene imine) [PEI]
  - used in detergents, adhesives, CO_2 extraction etc.
  - PEI has high charge density at low pH due to protonation

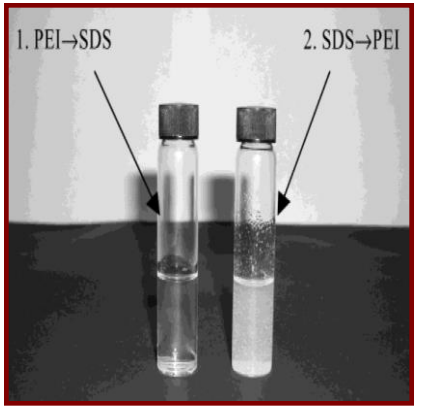




- <u>anionic surfactants</u>:
  - sodium dodecyl sulfate [SDS]
  - ubiquitous in shampoos & cleaning products
  - binds to oppositely charged polyelectrolytes

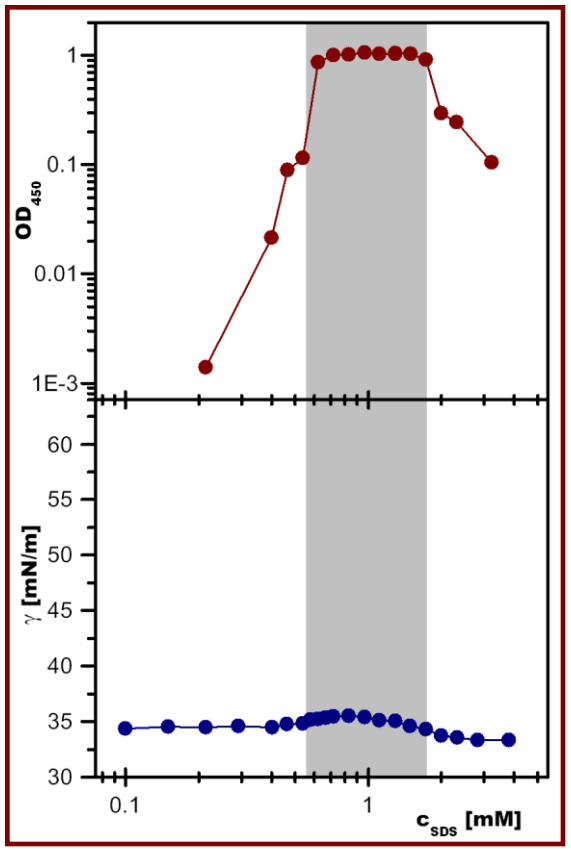


- <u>polyelectrolyte/surfactant mixtures</u>:
  - used in household products (cleaning, food etc.)
  - behavior interpreted by equilibrium self-assembly
  - bulk non-equilibrium effects are also important

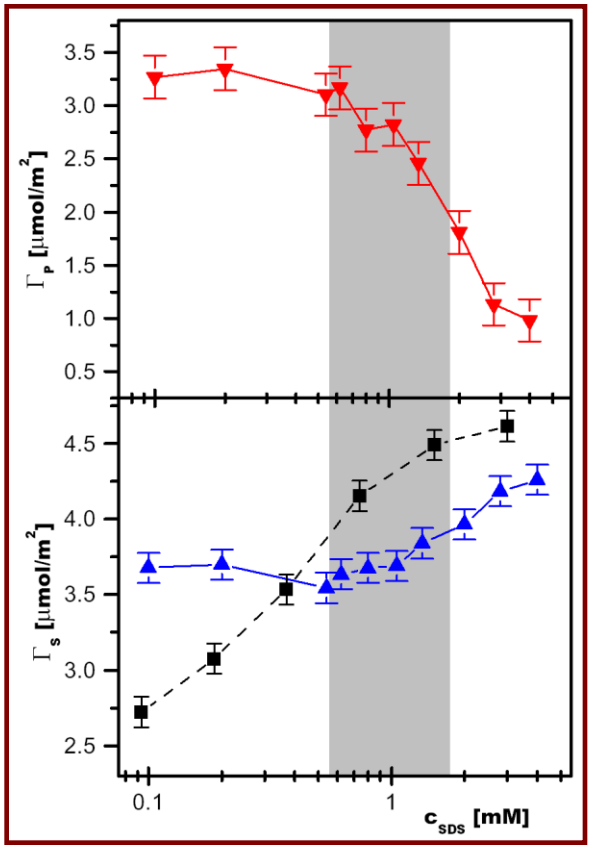


example 1: static air/liquid measurements of complex systems

(1) fresh-mixed

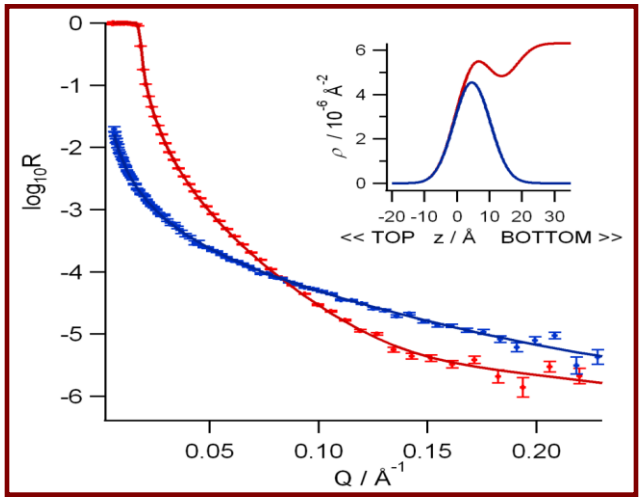


(2) aged-settled



(3) aged-redispersed

[Pdadmac] = 100 ppm
[SDS] = varied
[NaCl] = 100 mM



Campbell, Yanez, Angus-Smyth, Nylander & Varga, J Phys Chem B, 2011, 115, 15202

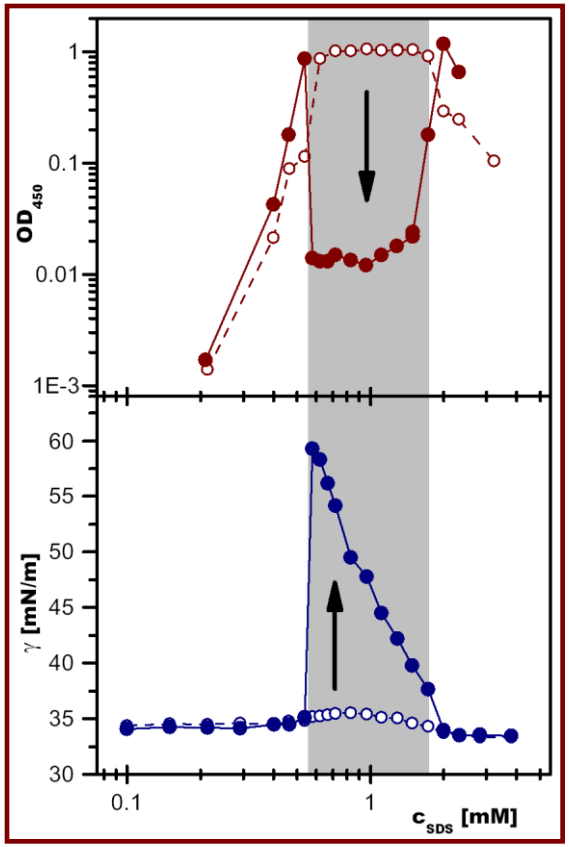
Campbell, Angus-Smyth, Yanez, Tonigold, Nylander & Varga, J Phys Chem Lett, 2010, 1, 3021

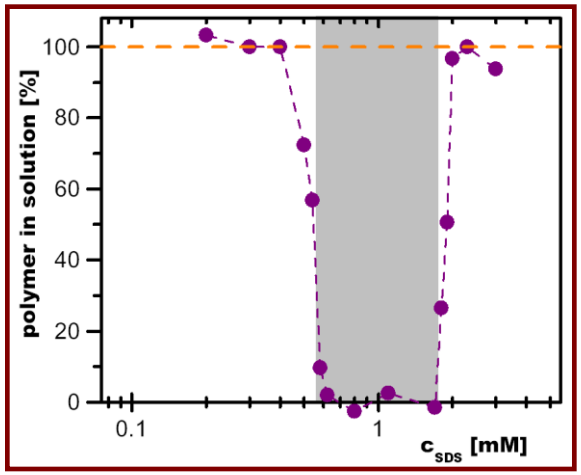
example 1: static air/liquid measurements of complex systems

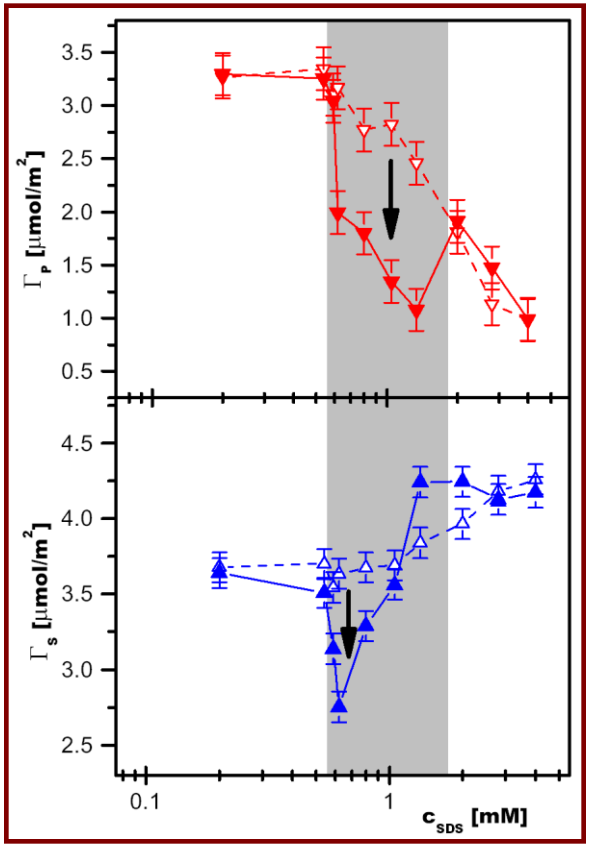
(1) fresh-mixed

(2) aged-settled

(3) aged-redispersed







Campbell, Yanez, Angus-Smyth, Nylander & Varga, J Phys Chem B, 2011, 115, 15202

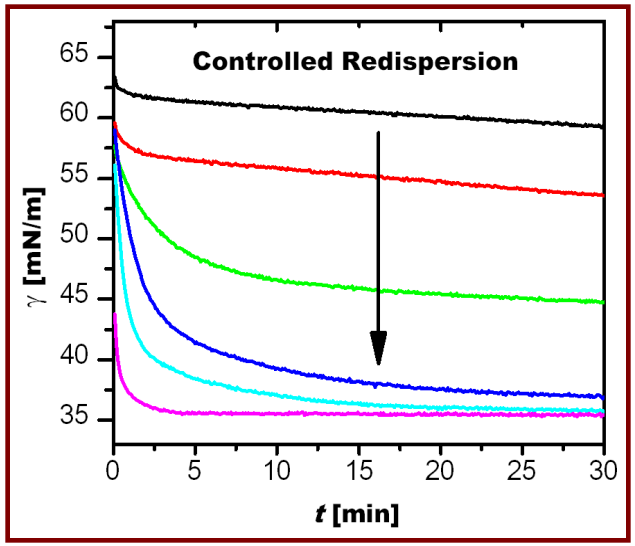
Campbell, Angus-Smyth, Yanez, Tonigold, Nylander & Varga, J Phys Chem Lett, 2010, 1, 3021

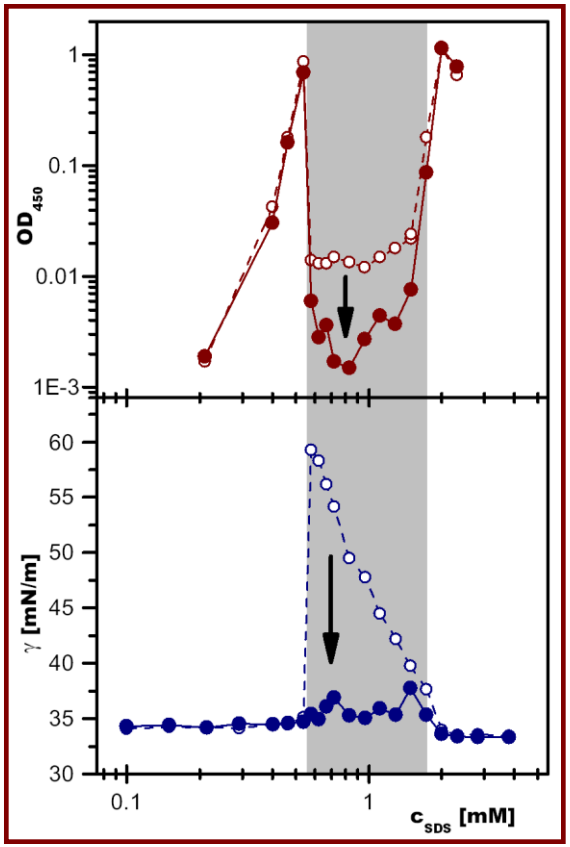
example 1: static air/liquid measurements of complex systems

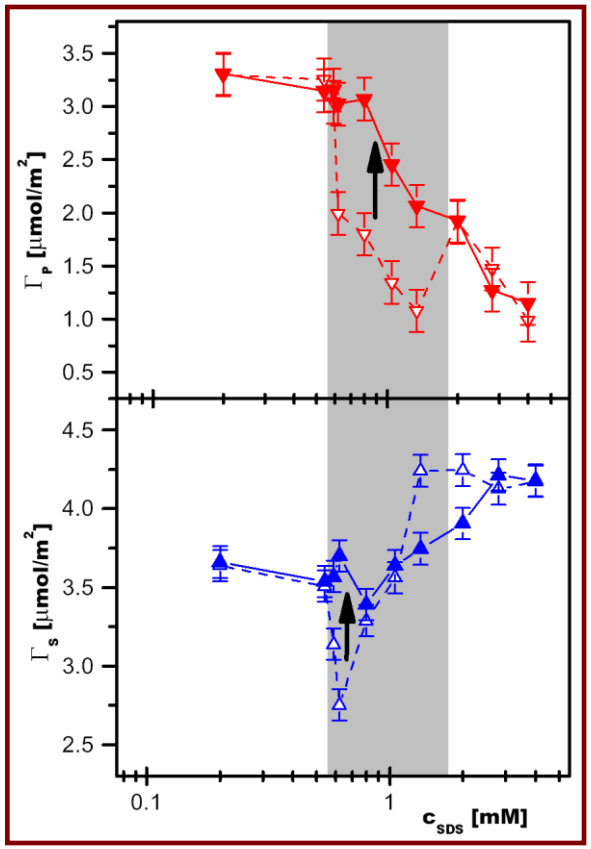
(1) fresh-mixed

(2) aged-settled

(3) aged-redispersed



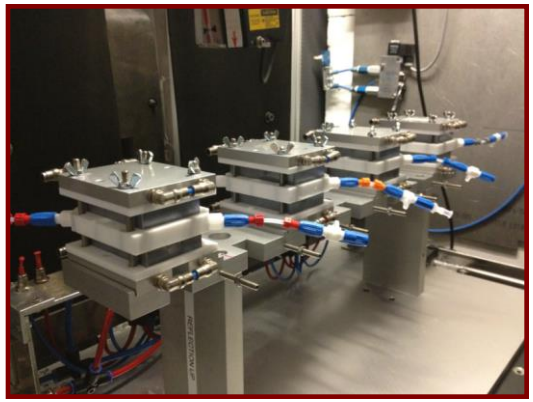




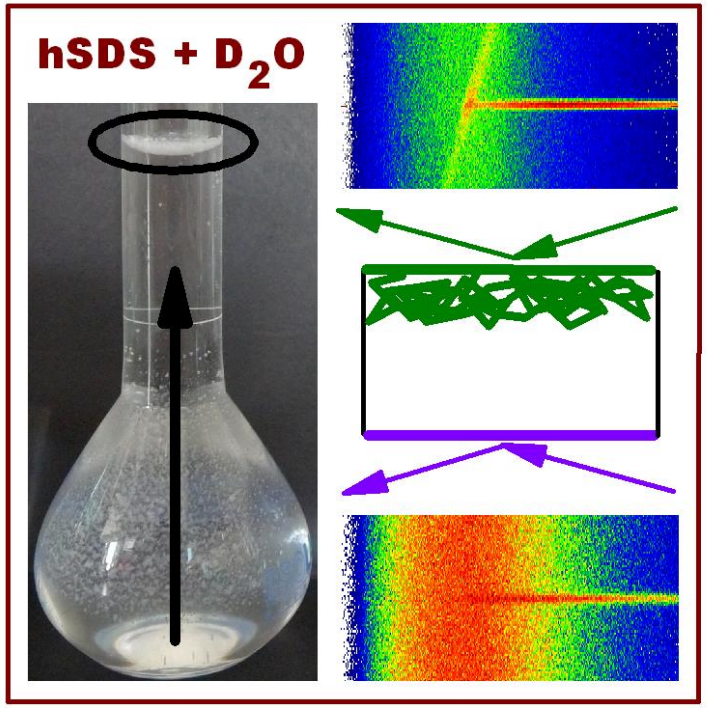
Campbell, Yanez, Angus-Smyth, Nylander & Varga, J Phys Chem B, 2011, 115, 15202

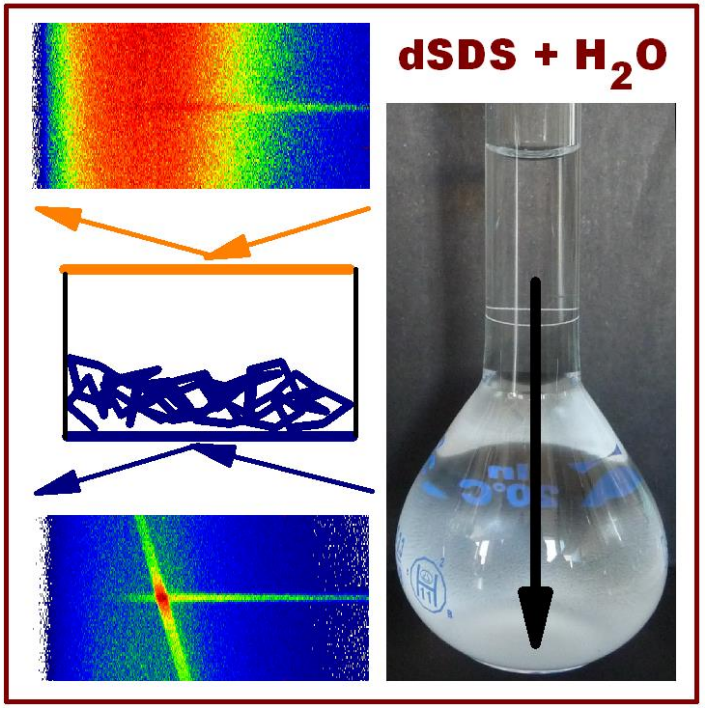
Campbell, Angus-Smyth, Yanez, Tonigold, Nylander & Varga, J Phys Chem Lett, 2010, 1, 3021

example 2: solid/liquid/solid measurements of complex systems



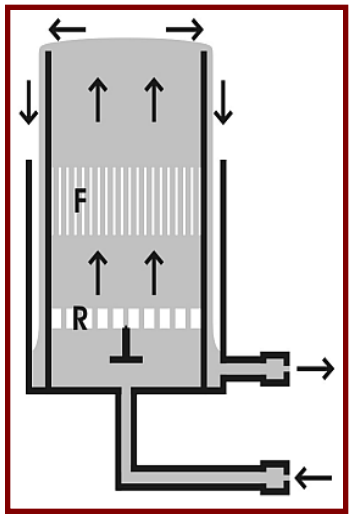
[Pdadmac] = 100 ppm
[SDS] = 0.82 mM
[NaCl] = 100 mM

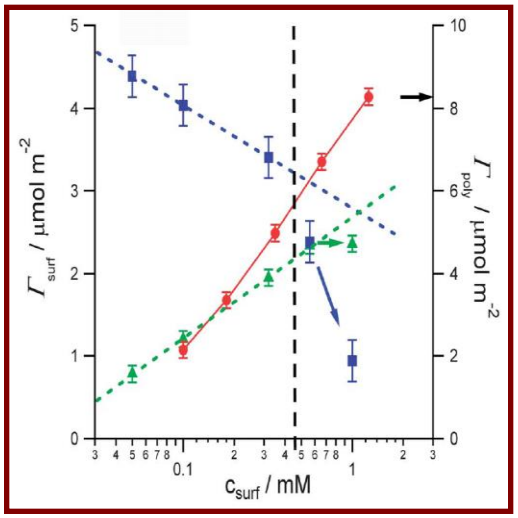


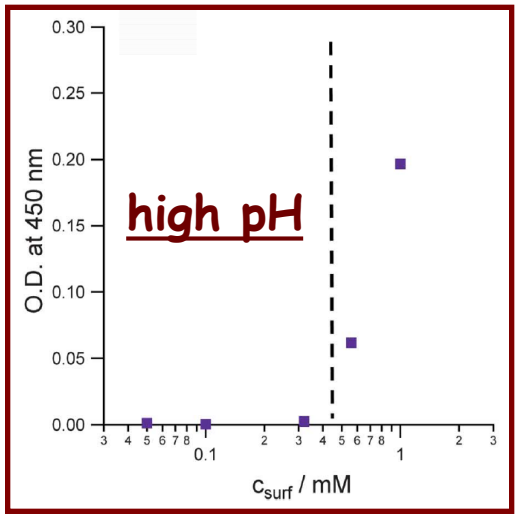


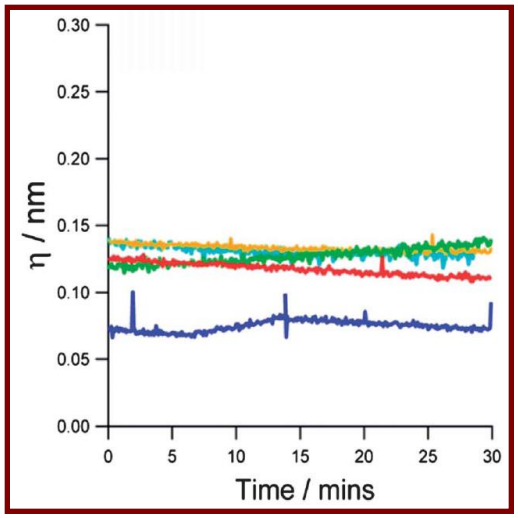
Campbell, Yanez, Angus-Smyth, Nylander & Varga, J. Phys. Chem. B, 2012, 116, 7981

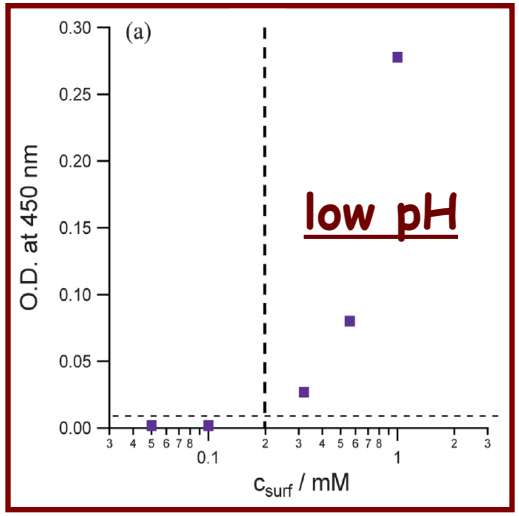
example 3: dynamic air/liquid measurements of complex systems

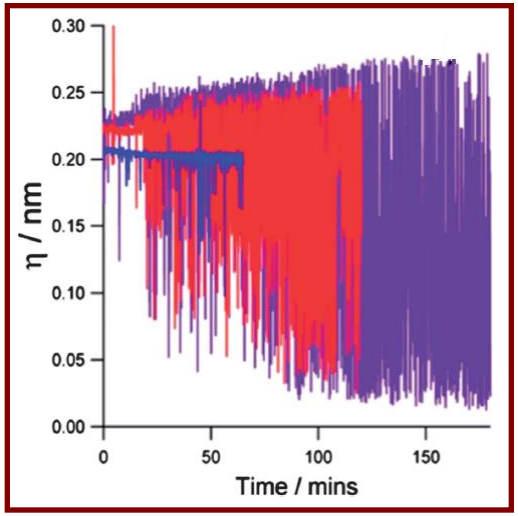








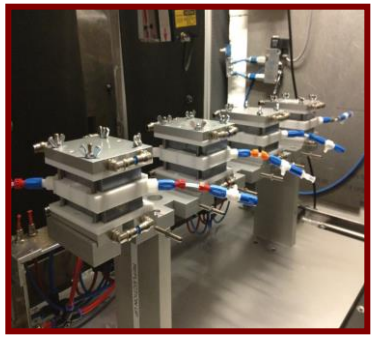




Angus-Smyth, Varga, Bain & Campbell, Soft Matter, 2013, 9, 6103

summary: ILL's platform to solve complex interfacial problems

- static air/liquid measurements:
  - non-equilibrium aggregates can be controlled to tune the surface properties
- solid/liquid/solid measurements:
  - surface properties from self-assembly modified by phase separation/gravity
- dynamic air/liquid measurements:
  - dynamic surface properties are seemingly uncorrelated with the static ones



- new platform for unique interfacial characterization at the ILL:
  - emerging as a center for resolving the surface behavior of complex mixtures