September 23-25, 2003, Florida State University, Tallahassee, Florida

NSFChemBio

Neutron Scattering for Chemistry and the Chemistry/Biology Interface

Joint Institute for Neutron Sciences Workshop Series

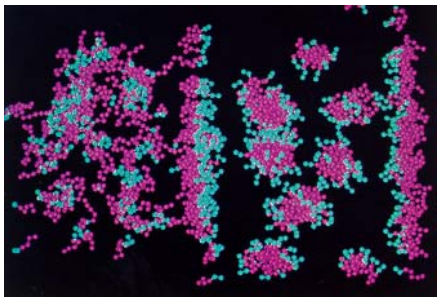
23-25th September 2003
Tallahassee, Florida

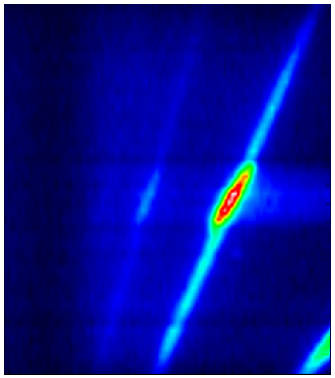
Studying Surfactant adsorption at interfaces by neutron reflectivity

The current 'state of the art' and future prospects

Jeff Penfold

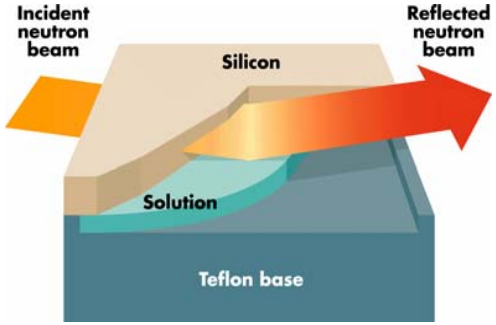
ISIS, CCLRC,
Rutherford Appleton Laboratory

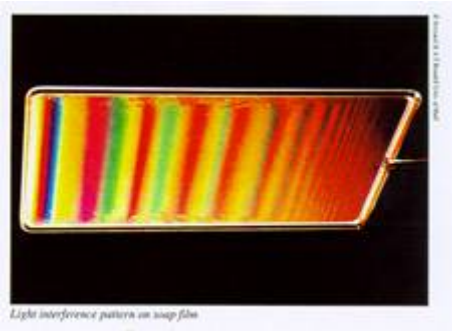




Specular reflection from surfaces and interfaces

DEPTH PROFILING : provides information about concentration / composition profiles normal to the interface





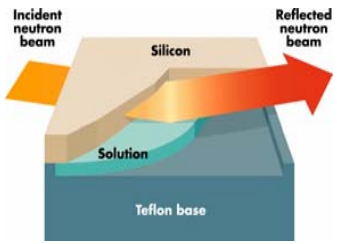
Analagous to optical interference, ellipsometry

- **Manipulate Refractive Index**
- **Penetrating probe**
- **In-situ, non-destructive**
- **Require optical quality surfaces**

- **complex multi-component systems**
- **buried interfaces**
- **difficult environments**

(Penfold, Thomas, J Phys: Condens Matt 2 (1990) 1369, T P Russell, Mat Sci Rep 5 (1990) 171)

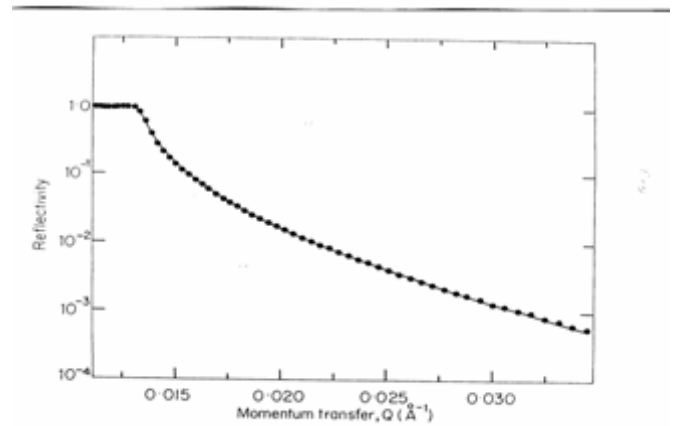
Specular Neutron Reflection



Within the Born Approximation

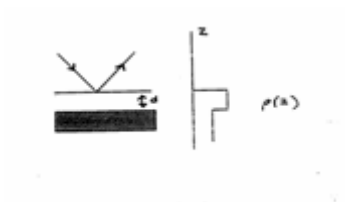
$$R(Q) = \frac{16\pi^2}{Q^2}\left|\int \rho(z)e^{iQz}dz\right|^2$$

$$Q = k_1 - k_0 = 4\pi \sin\theta / \lambda$$

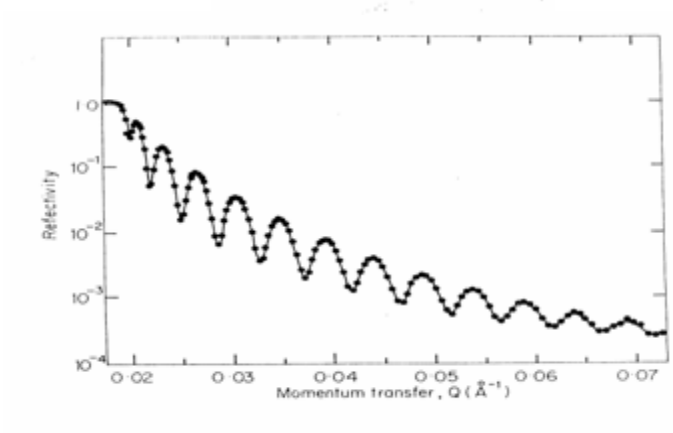


Refractive index, n

$$n = 1 - \lambda^2 A - i\lambda B$$



For a thin film at the interface, see interference which can be described exactly using thin film optics formulism



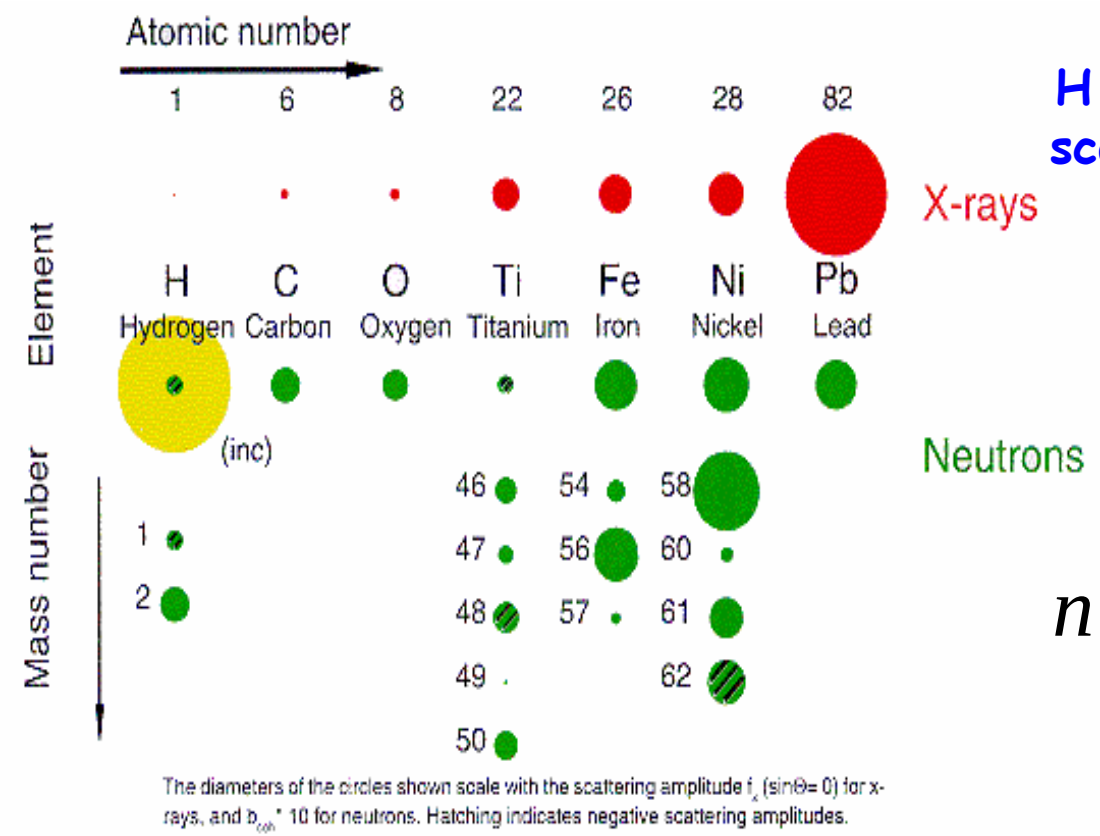
$$R(Q) = \left|\frac{r_{12} + r_{23}e^{-2i\beta}}{1 + r_{12}r_{23}e^{-2i\beta}}\right|$$

$$r_{ij} = \frac{(p_i - p_j)}{(p_i + p_j)}$$

$$p_i = n_i \sin\theta_i$$

$$\beta = {}^{2\pi}\!/_{\lambda}\, n_i d_i \sin\theta_i$$

Contrast variation (H/D isotopic substitution)



H and D have vastly different scattering powers for neutrons

$$n = k_1 / k_0$$

$$n = 1 - \lambda^2 A - i\lambda B$$

$$A = N b / 2\pi$$

Extensively use H/D isotopic substitution to manipulate 'contrast' of refractive index

Off-Specular Scattering

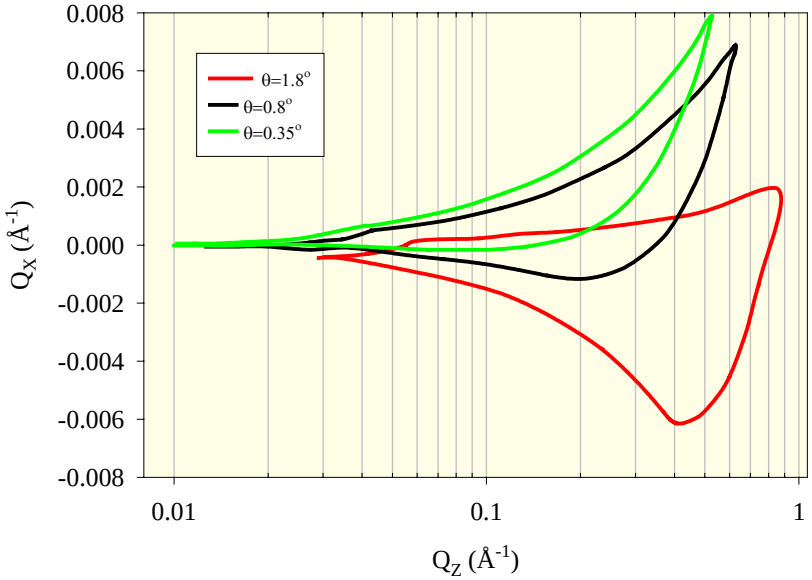
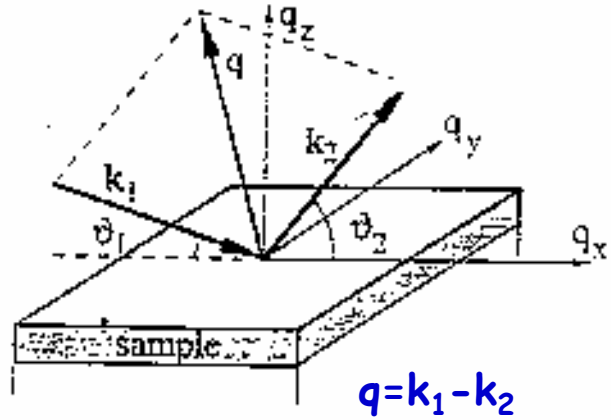
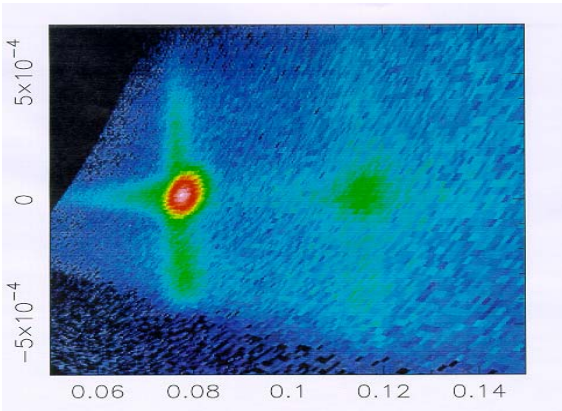


Figure 1. The accessible wave-vector range for a series of incident angles for the current SURF geometry.



$q=k_1-k_2$
$q_z=2k\sin\theta$
$q_x=k(\cos\theta_1-\cos\theta_2\cos\psi)$
$q_y=k\cos\theta_1\sin\psi$

ψ is angle out of plane



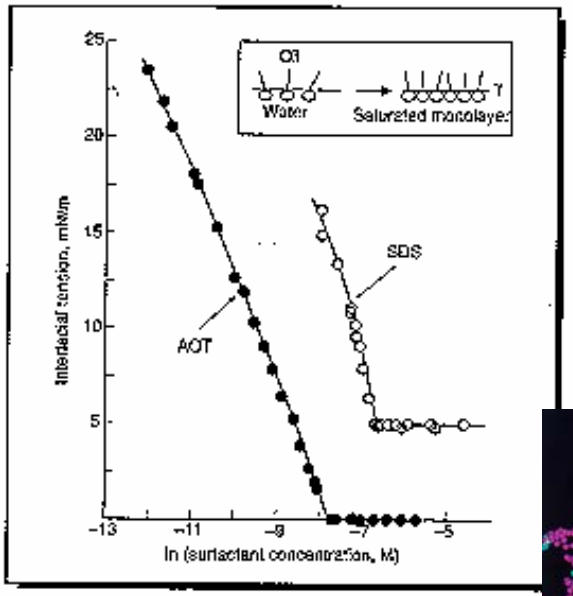
(Sinha et al, Phys Rev B 38 (1988) 2297)

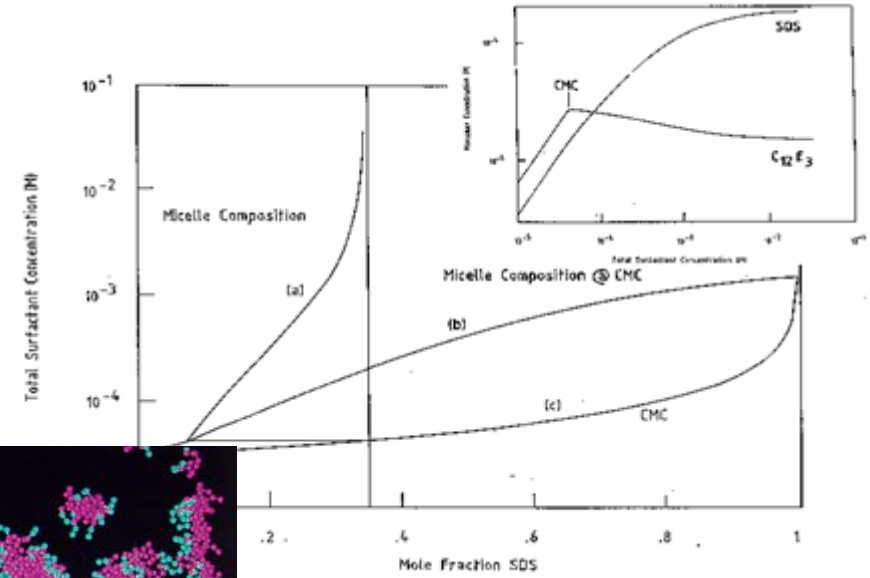
In Distorted Wave Born Approximation, DWBA

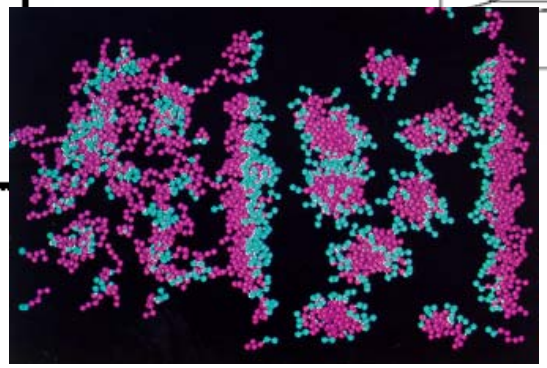
$$\left.\frac{d\sigma}{d\Omega}\right)_{diff} = N^2 b^2 L_x L_y \left|T_i(k_i)\right|^2 \left|T_r(k_r)\right|^2 S(q)$$

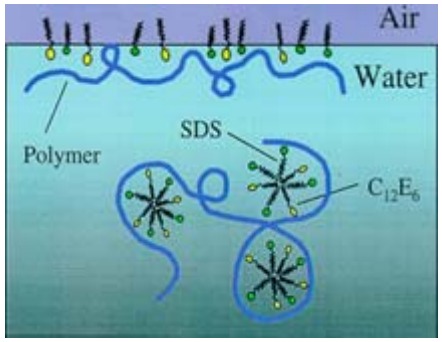
$$S(q) = \frac{1}{|\alpha|^2} e^{-\left(\alpha^2-\alpha^{*2}\right)\sigma^2/2} \int dx \int dy e^{iq.\rho}\left(e^{|\alpha|^2 C(x,y)} - 1\right)$$

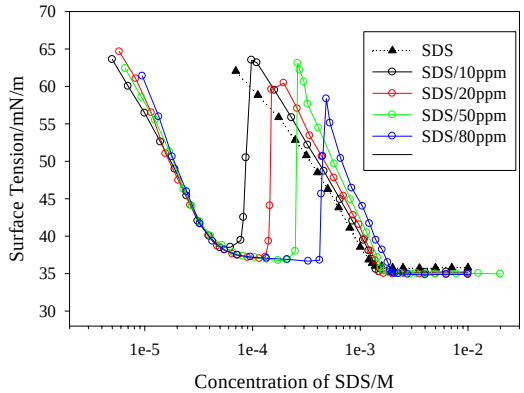
Surfactant Adsorption at Interfaces

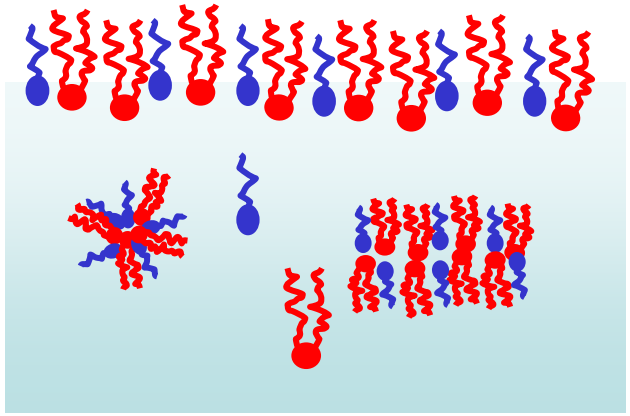












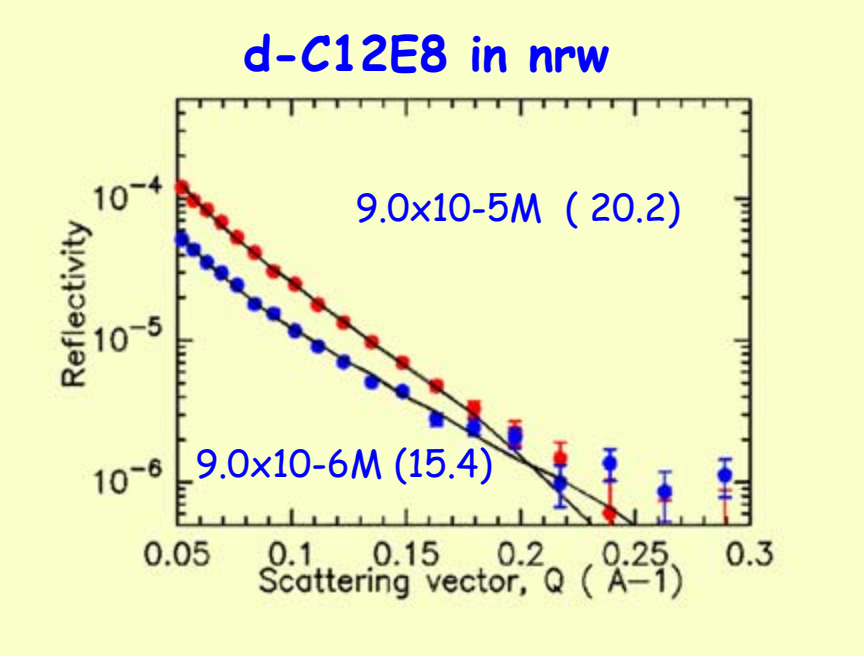
Lu, Thomas, Penfold, Adv Coll Int Sci 84 (2000) 143-304

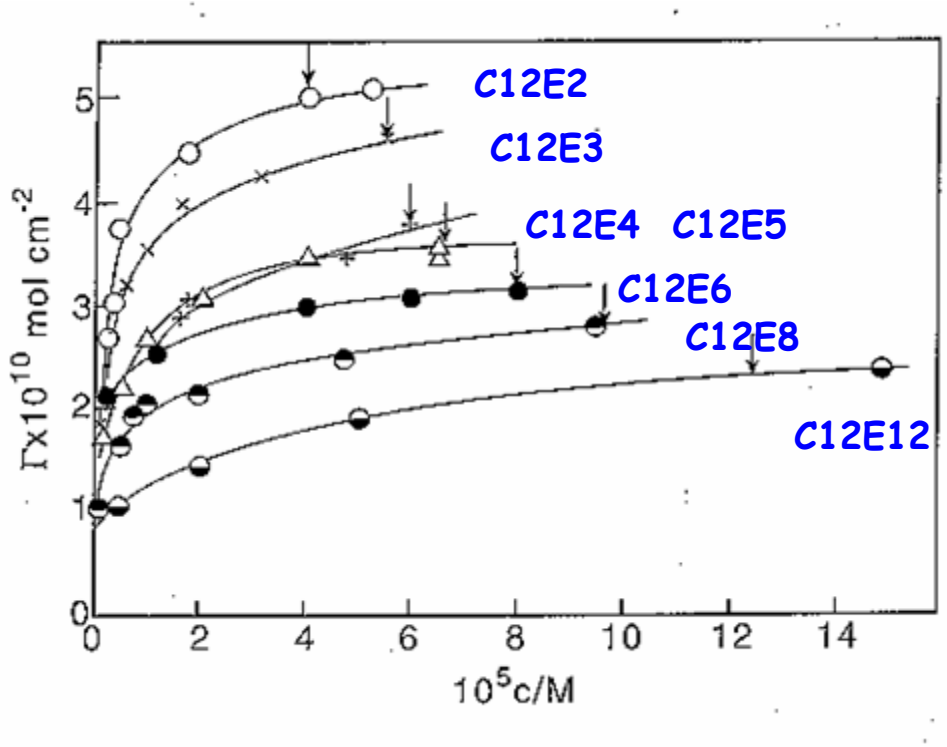
Measurement of Adsorbed Amount

For deuterated surfactant in null reflecting water, the reflectivity arises only from adsorbed surfactant layer

Assuming that the reflectivity can be described by a single uniform layer then the adsorbed amount is

$$A = \frac{\sum b}{d\rho}$$



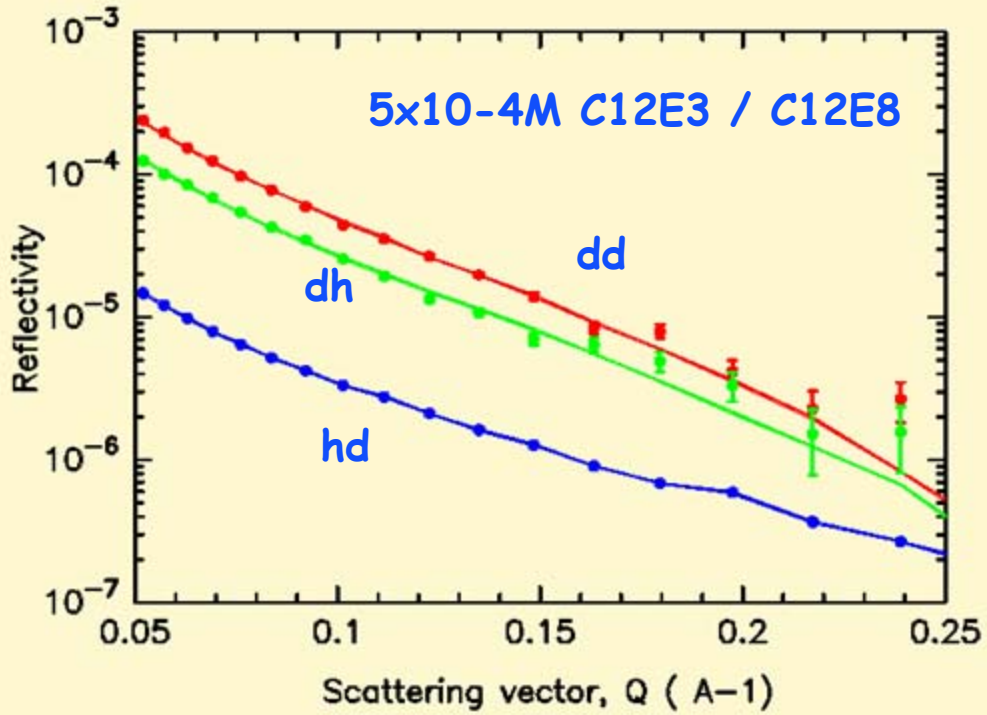


Non-ionic adsorption (C12E2 to C12E12)

Adsorption of mixed surfactants at interfaces

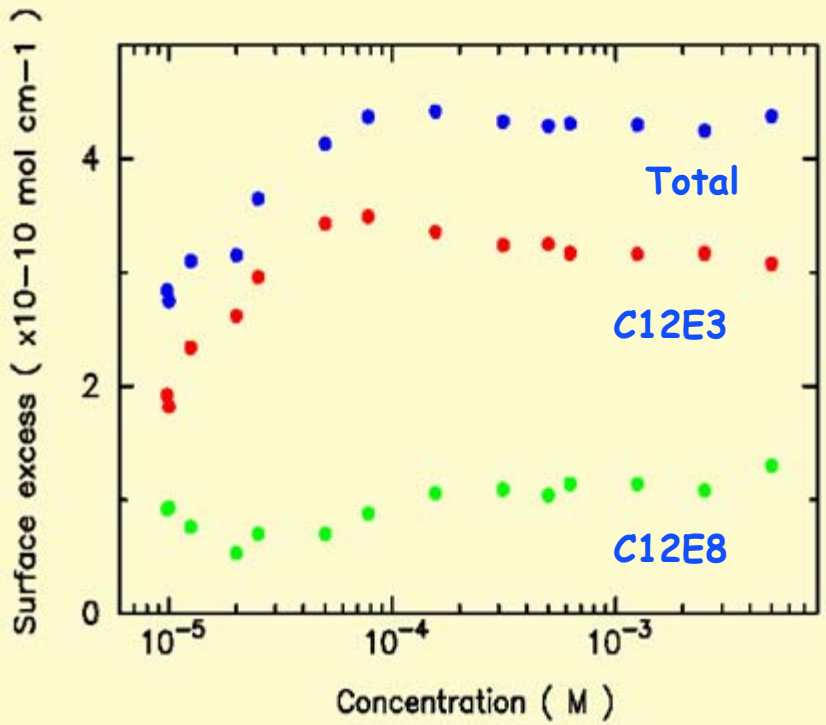
For binary mixture selectively deuterate each component in turn

dd total adsorption
dh C12E3
hd C12E8



$$d\rho = \sum b_1 / A_1 + \sum b_2 / A_2$$

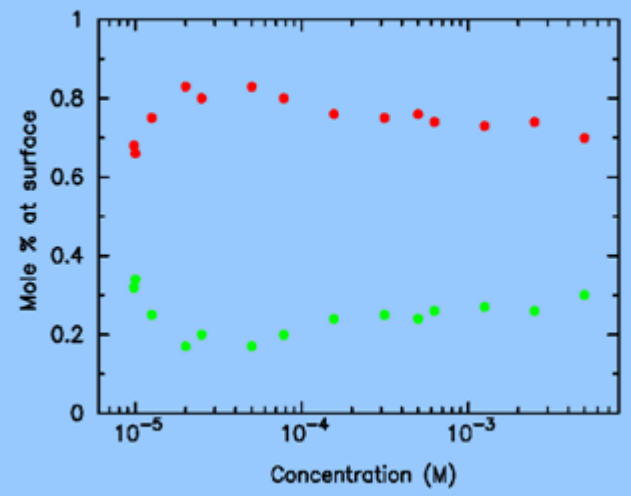
Adsorption of C12E3 / C12E8 mixture at the air-water interface



Adsorbed amounts

50/50 C12E3 / C12E8

Close to ideal mixing
Simillar alkyl chain but very different head group size



Composition

First experimental verification of abrupt change in composition at CMC

J Penfold, E Staples, L Thompson, I Tucker, Coll Surf A 102 (1995) 127

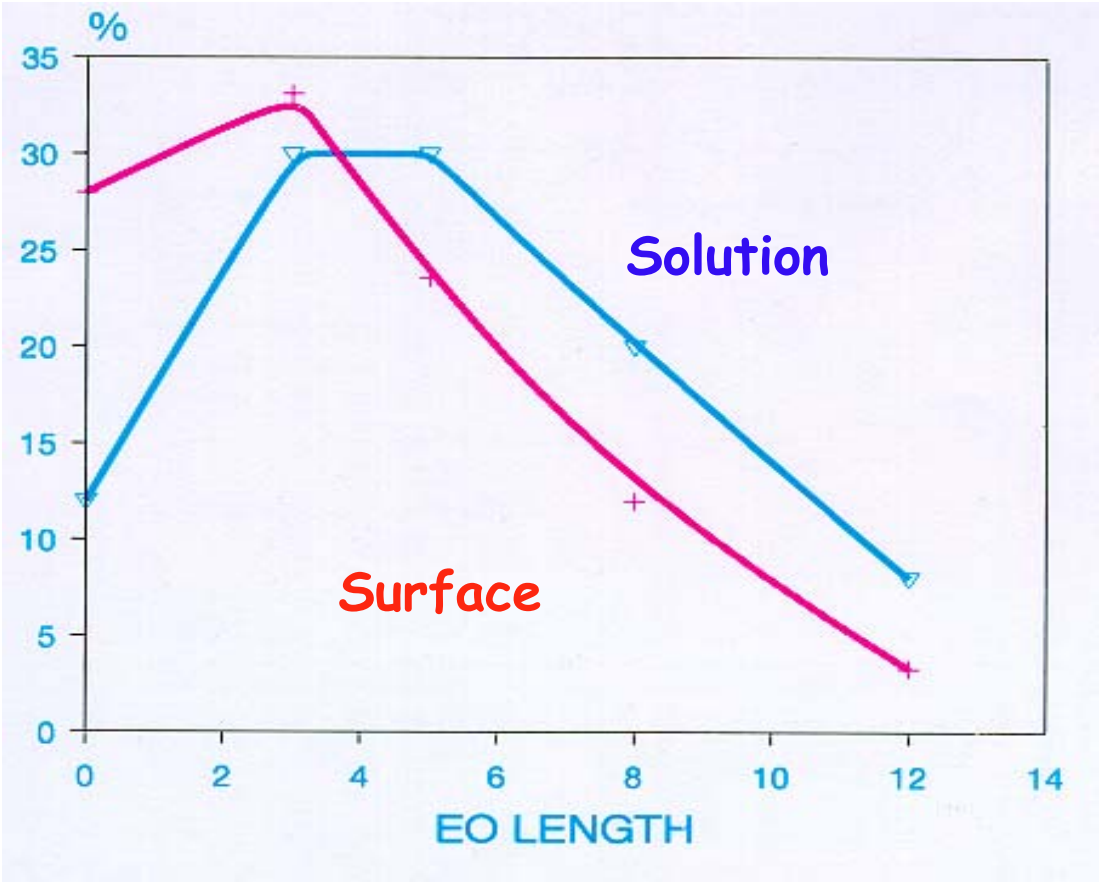
Surface adsorption in complex multi-component mixtures

90% C12E5 / 10% SDS / 0.01M NaCl

Comprising of Dodecanol, C12E3, C12E5, C12E8, and C12E12

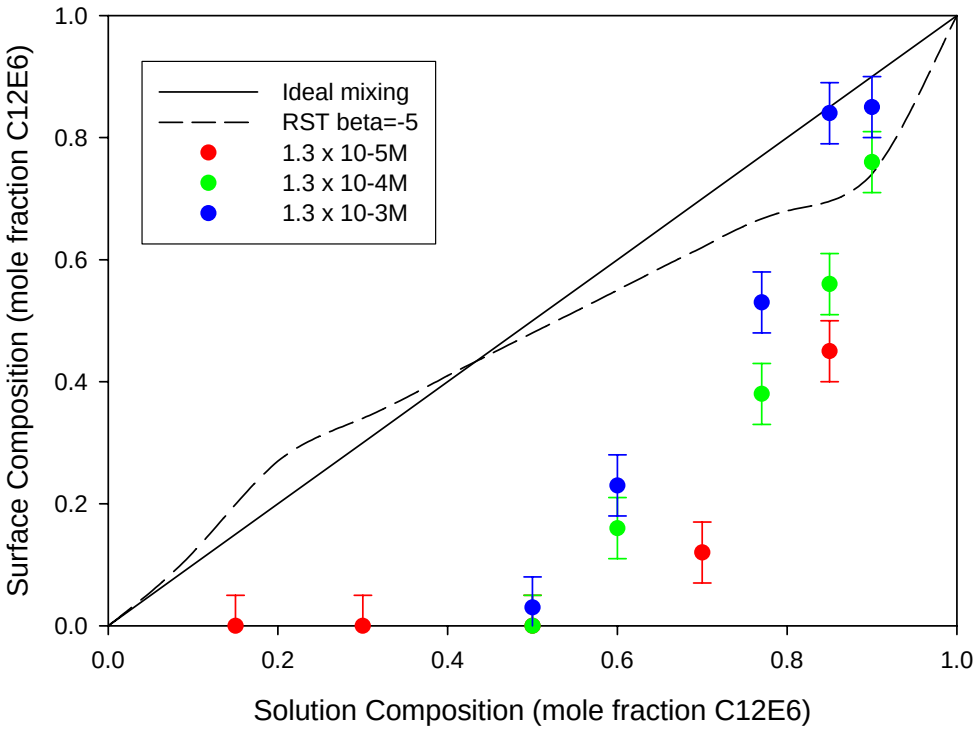
for c>>CMC

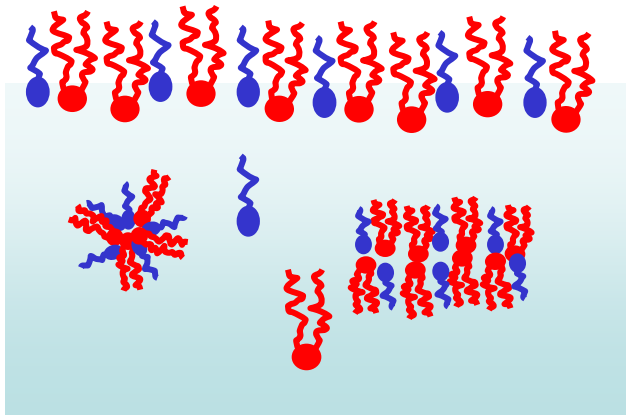
E Staples, L Thompson, I Tucker, J Penfold, Langmuir 10 (1994) 4136



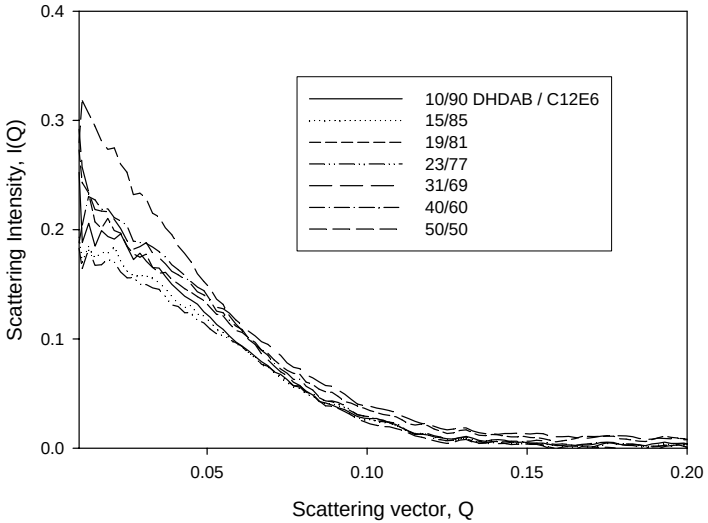
Solution composition EO 5.0, surface EO 3.6
Mixture adsorption ~ 40% greater than for SDS / C12E5

DHDAB / C12E6 surface composition (solution conc)





Changes in bulk phase behaviour mediating changes in monomer conc

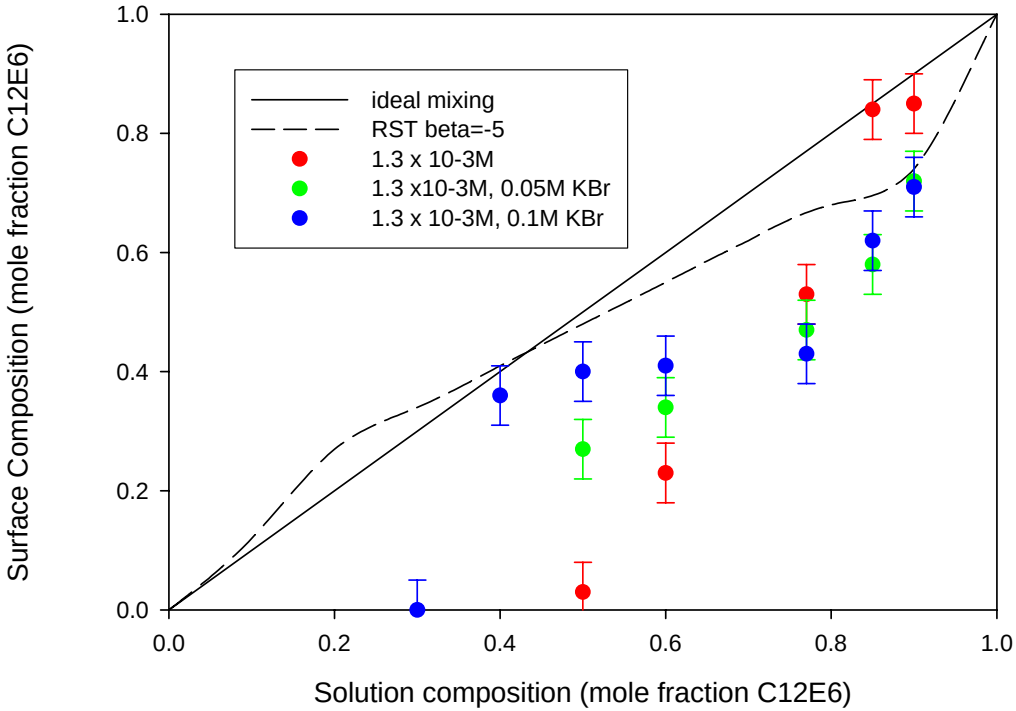


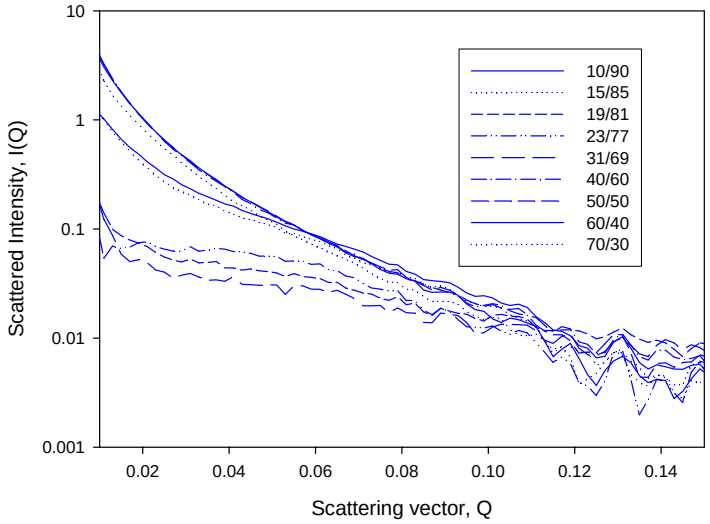
See extreme departure from ideality which cannot be accounted for by existing theories or structural changes in surface layer on mixing

Globular micelles for C12E6 rich compositions, N increases with nonionic content

Transition to lamellar phase @ ~ 50/50 composition. Aggregate composition close to solution composition

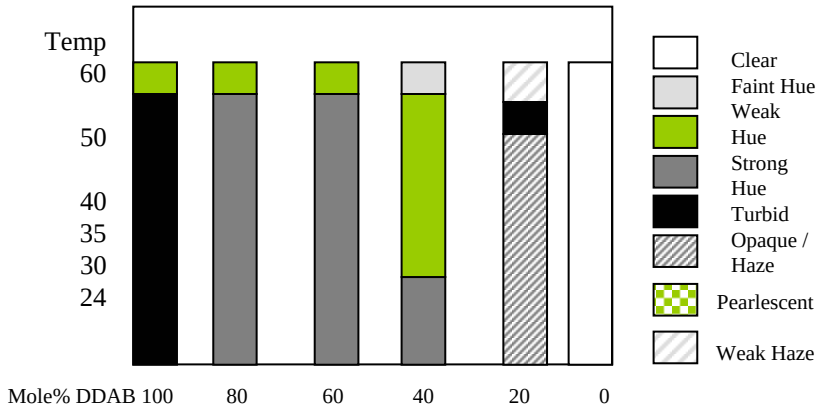
1.3 x 10-3M DHDAB / C12E6 surface composition (salt conc)





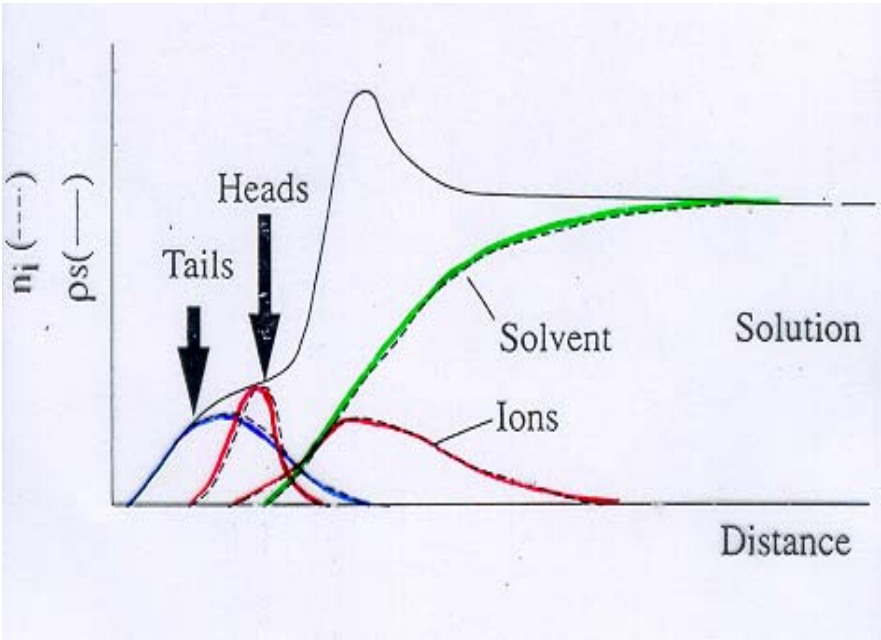
Cationic rich, large lamellar fragments (for >40% DHDAB)
Nonionic rich, large elongated micelles

Region of co-existance of lamellar phase and globular micelles coincident with plateaux in surface composition



Absolute value of scattering from globular micelles (90/10 to 30/60) implies co-existence region

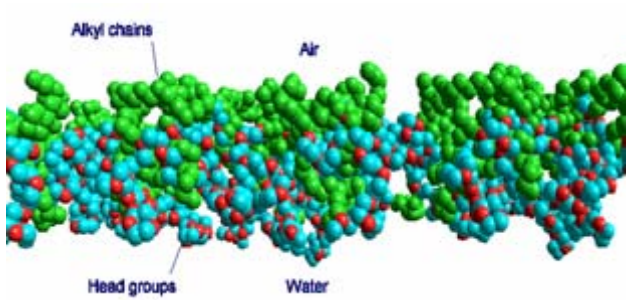
Structure of the adsorbed surfactant layer



$$R(\kappa) = \frac{16\pi^2}{\kappa^2}\left|\int_{-\infty}^{+\infty} \rho(z) e^{-i\kappa z} dz\right|$$

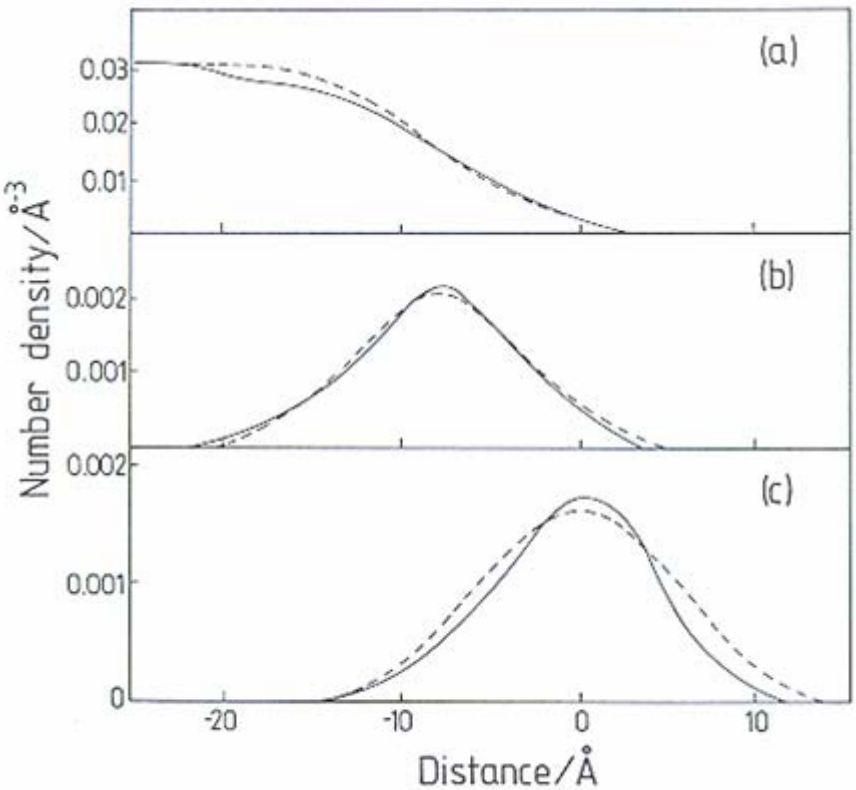
$$\rho(z) = b_c n_c(z) + b_h n_h(z) + b_s n_s(z)$$

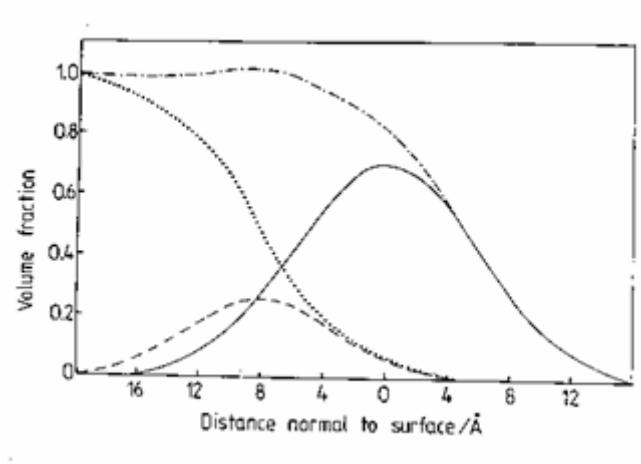
$$R(\kappa) = \frac{16\pi^2}{\kappa^2}\left[b_c^2 h_{cc} + b_h^2 h_{hh} + b_s^2 h_{ss} + 2b_c b_h h_{ch} + 2b_c b_s h_{cs} + 2b_h b_s h_{hs}\right]$$

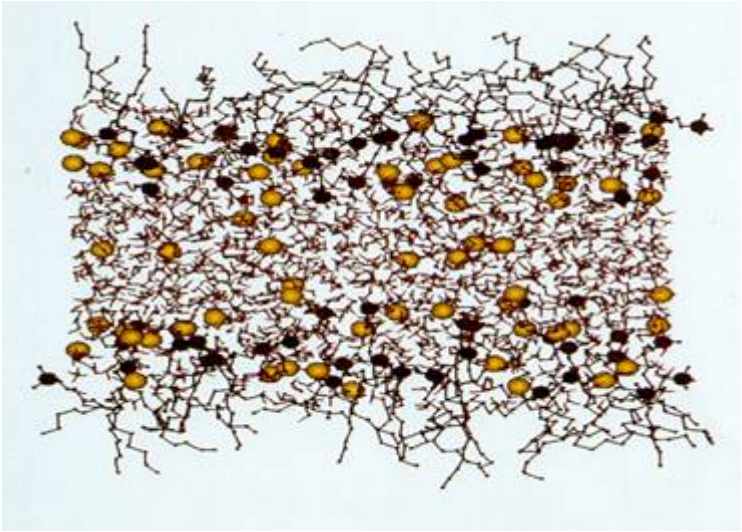


Partial Structure Factors

Structure of adsorbed surfactant layer of $C_{16}TAB$



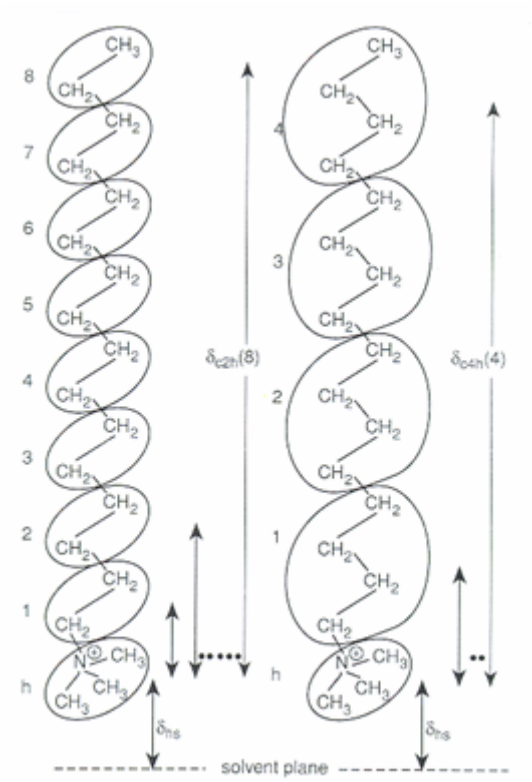




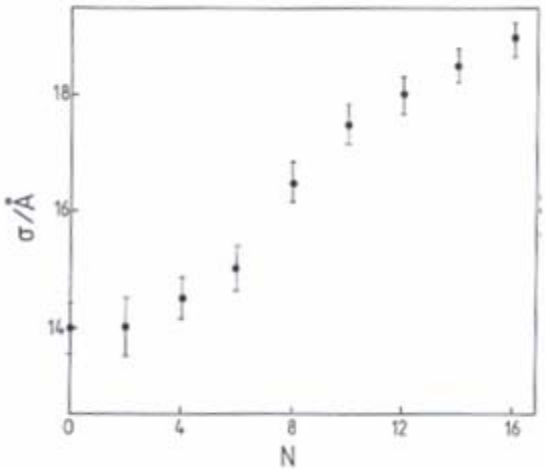
C_{16}TAB Structure

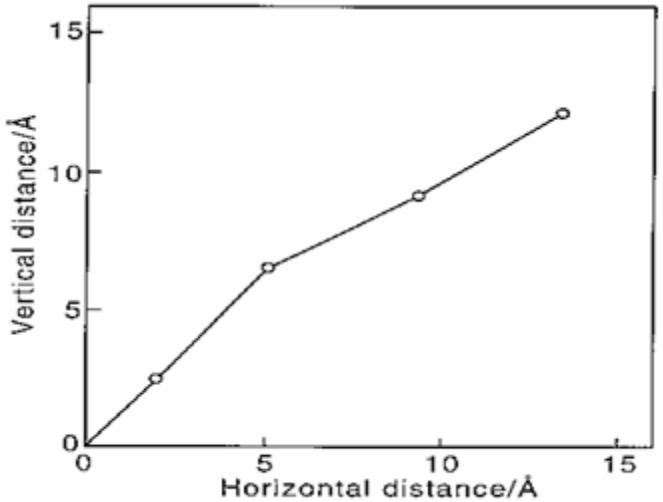
(Lu, Li, Smallwood, Thomas, Penfold, J Phys Chem 99 1995 8233)

From more detailed labelling obtain a finer description of the structure of the adsorbed layer



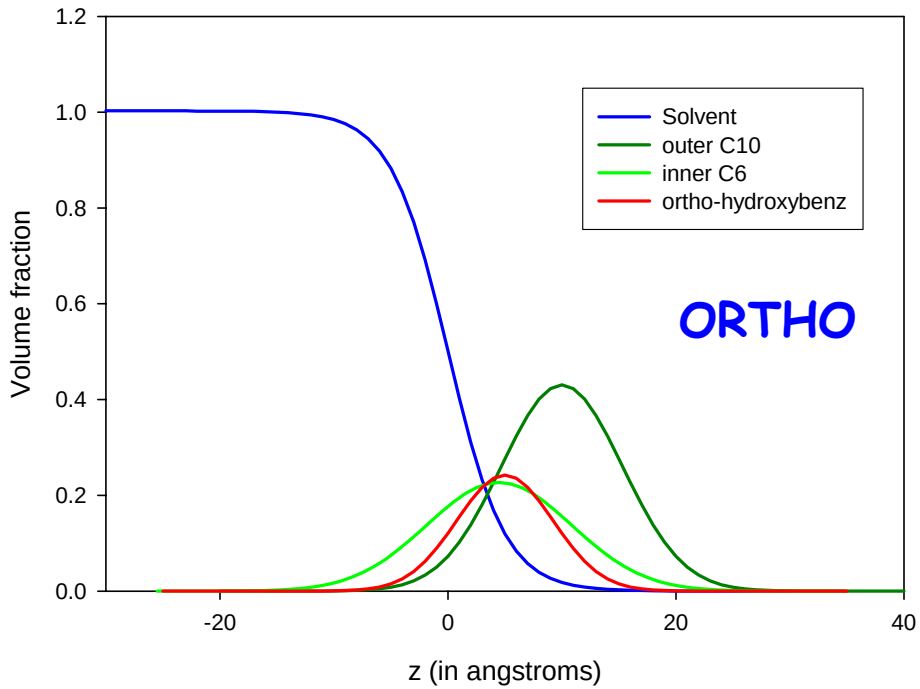
Measurements with decreasing size of the labelled fragment gives a direct estimate of the capillary wave contribution to the widths of the distributions





From labelling groups of 2 or 4 methylenes compared to headgroup or solvent can map out mean configuration of the chain

Adsorption of aromatic counter-ions: role of isomeric form



C16TAB + ortho (para) hydroxybenzoate

Ortho induces massive growth to large highly elongated flexible micelles; Para does not

2mM C16TAB / 12mM hbz

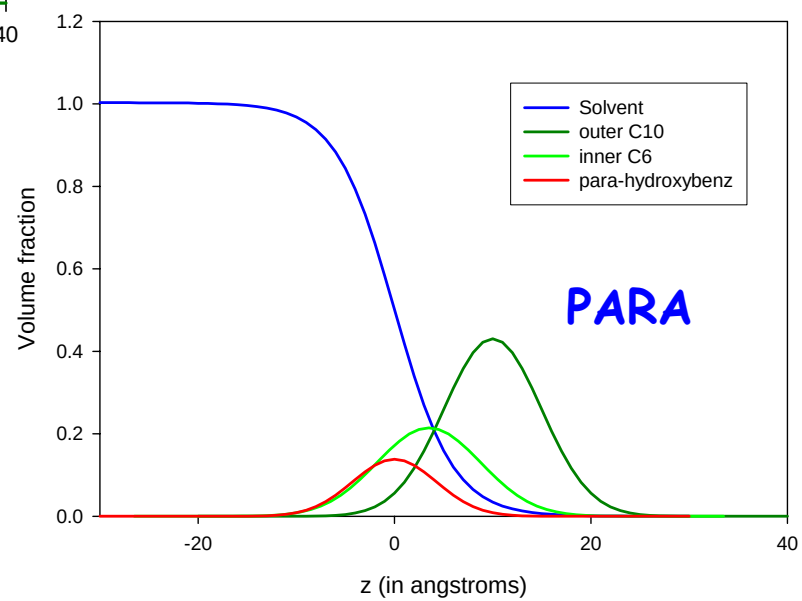
Ortho:

No of counterions / surfactant anion ~ 0.85
Counterion in hydrophobic environment

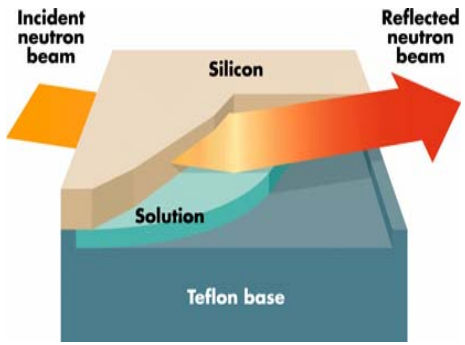
Para:

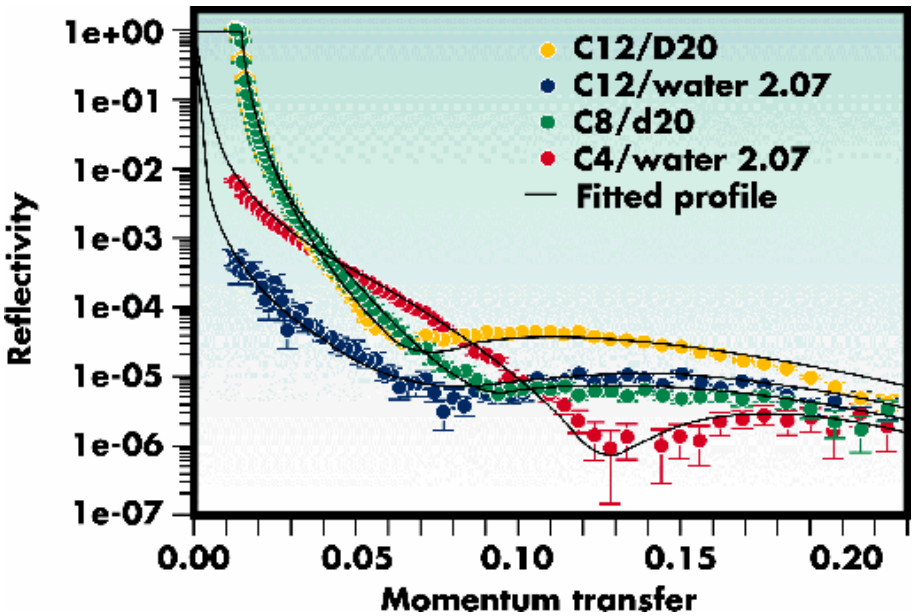
No of counterions / surfactant anion – 0.5
Counterion in hydrated headgroup region

From simple packing criteria, V/Al, and assuming V~430, l~21.7, A~55, V/Al increases from ~0.35 to ~0.5 if V increases to 600 for ortho isomer



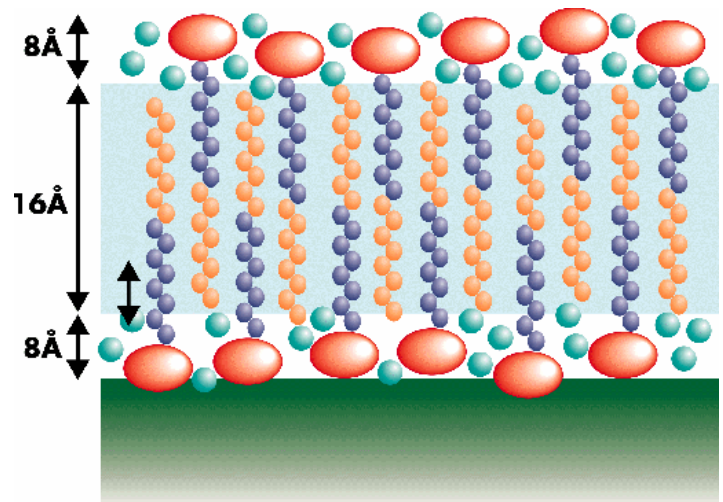
Surfactants at the solution-solid interface





(Fragnetto, Thomas, Rennie, Penfold, Langmuir 1996 12 6036)

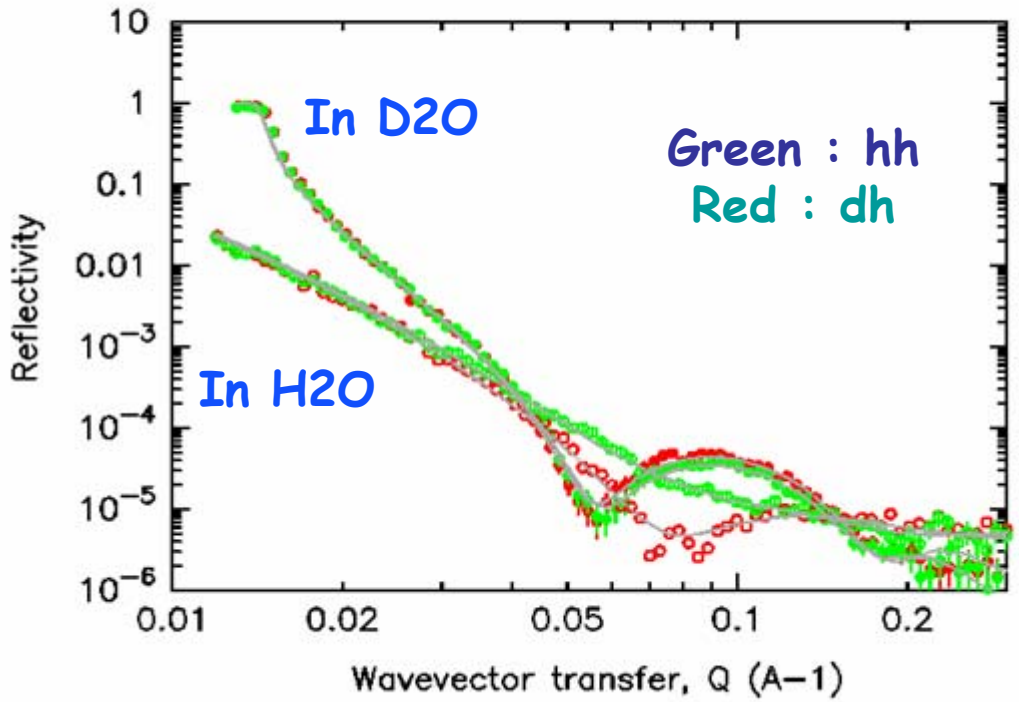
Detailed surface structure from labelling



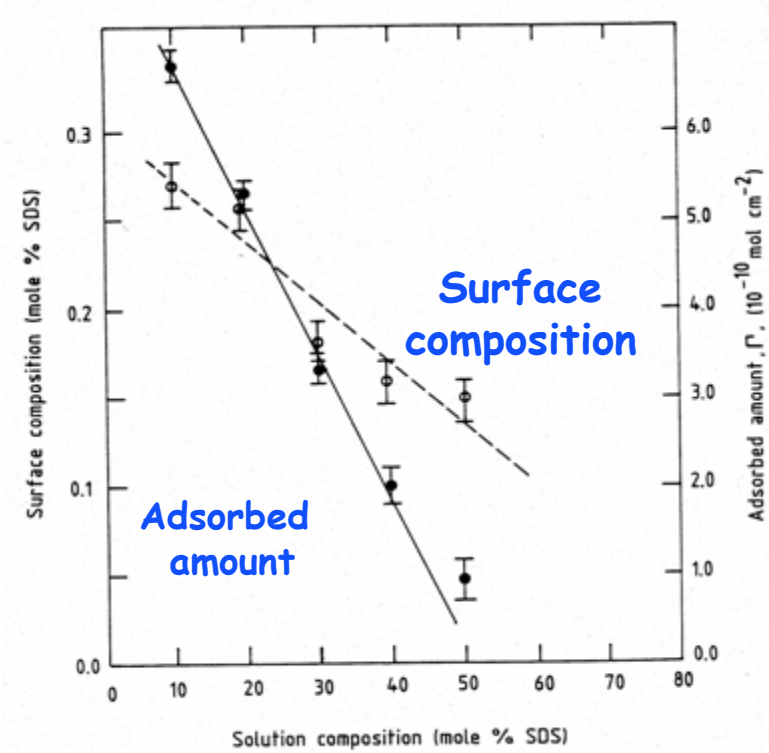
Fragmented bilayer or flattened micellar structure

Only indirect information about in-plane structure

10^{-3}M 20/80 SDS / C12E6 at hydrophilic silica / solution interface



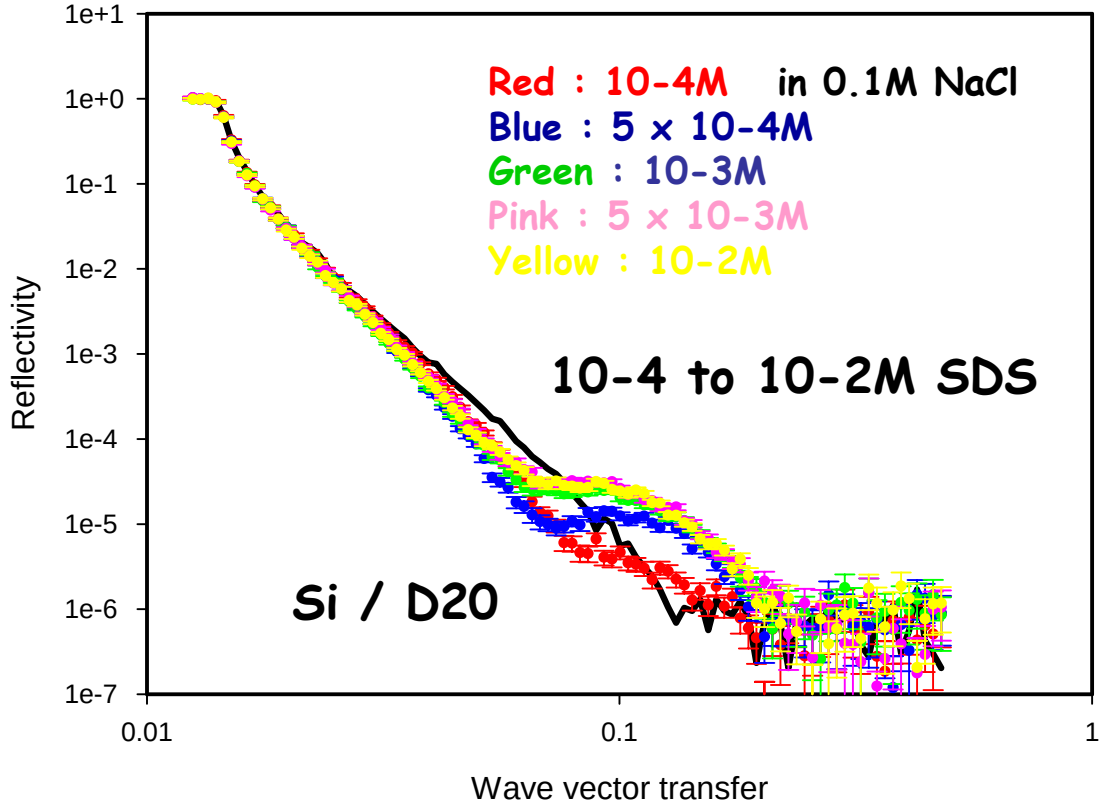
No adsorption for solutions compositions rich in SDS, > 50/50



Adsorption markedly modified by relative affinity of the two different surfactants for the surface

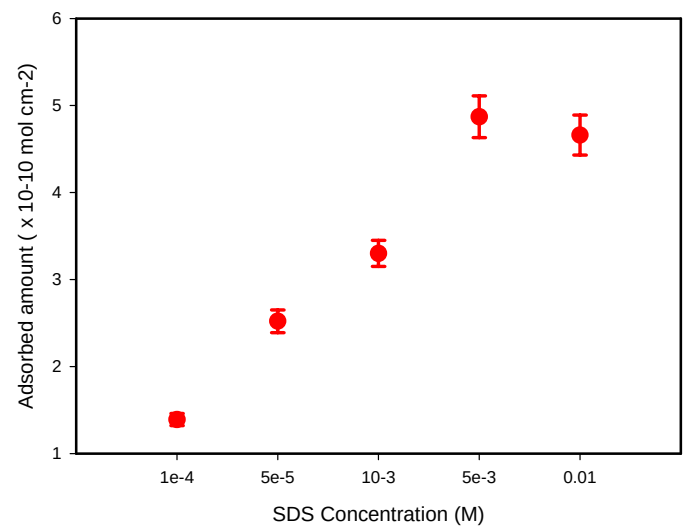
Penfold, Staples, Tucker, Thomas, Langmuir, 18 (2002) 5755)

SDS adsorption onto poly-dmdaac coated surface



$$\Gamma = \frac{d}{NV}\left(\frac{\rho_s - \rho_f}{\rho_s}\right)$$

SDS Isotherm



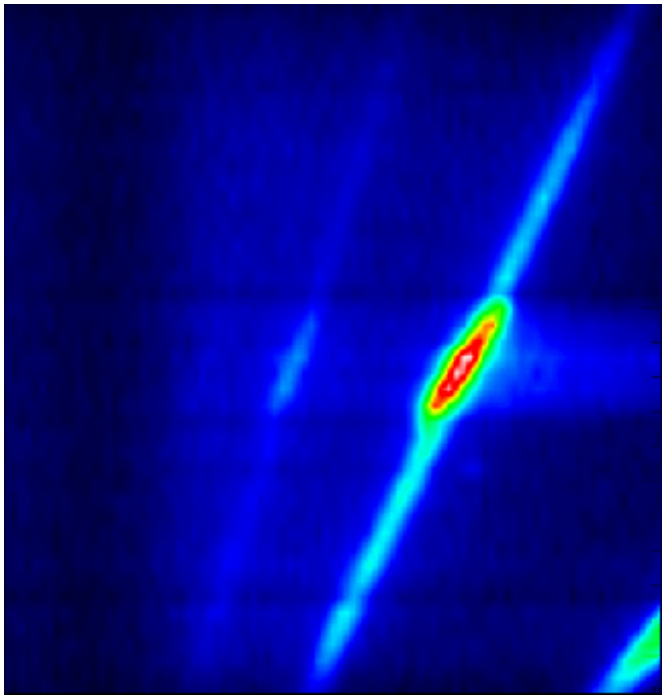
- Thin polymer layer at interface
- Polymer layer remains intact
- Strong SDS adsorption
- SDS layer ~ 36 to 40 angstroms

Adsorption at plateaux similar to that at A/W interface

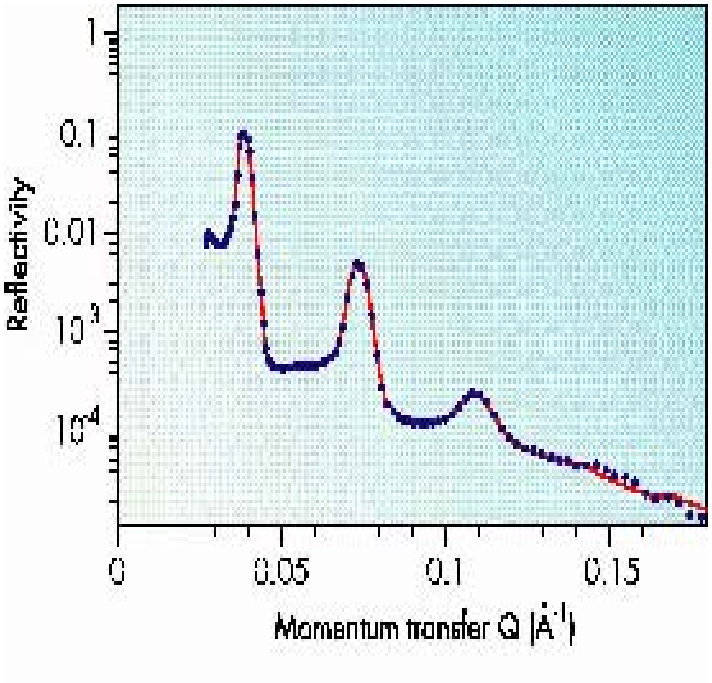
Surface ordering in Surfactant systems

(Li, Weller, Thomas, Rennie, Webster,Penfold, Heenan, Cubitt, J Phys Chem 103 (1999) 10800)

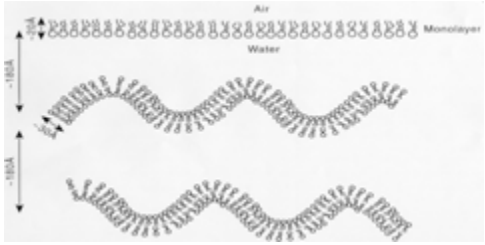
2% AOT / D2O



See well-defined 'Bragg peaks' associated with surface lamellar ordering, extending ~1 micron into the bulk solution



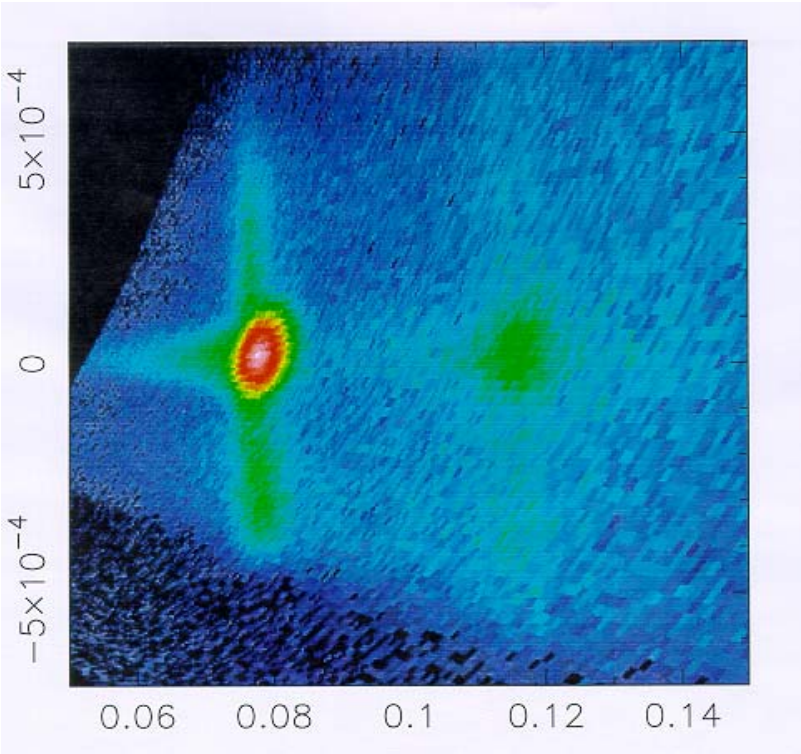
Observe strong 'off-specular' scattering at constant Qz.

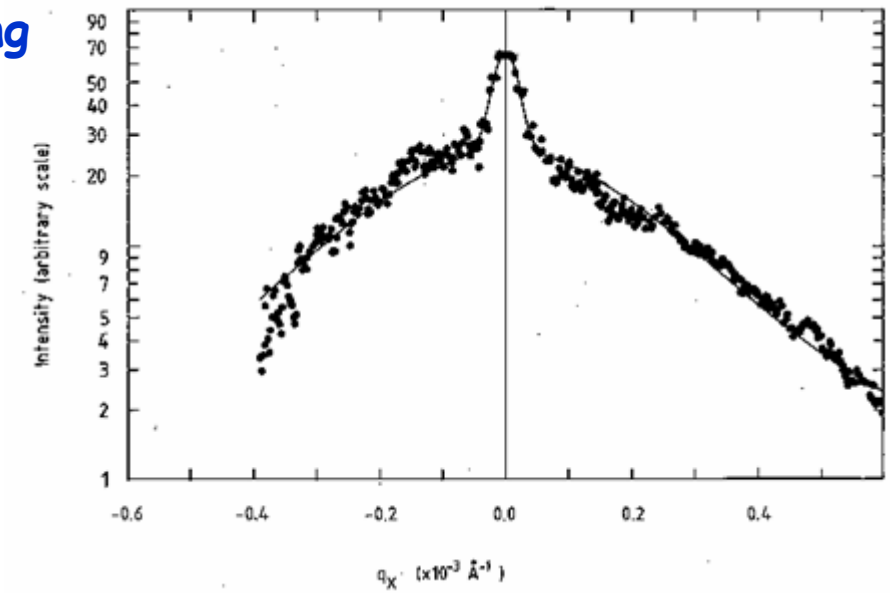


Attributed to conformal roughness caused by 'Helfrich waves' in the surface ordered lamellar bilayers

2% h-AOT / D2O at A/W interface (25c)

Constant Qz off-specular scattering

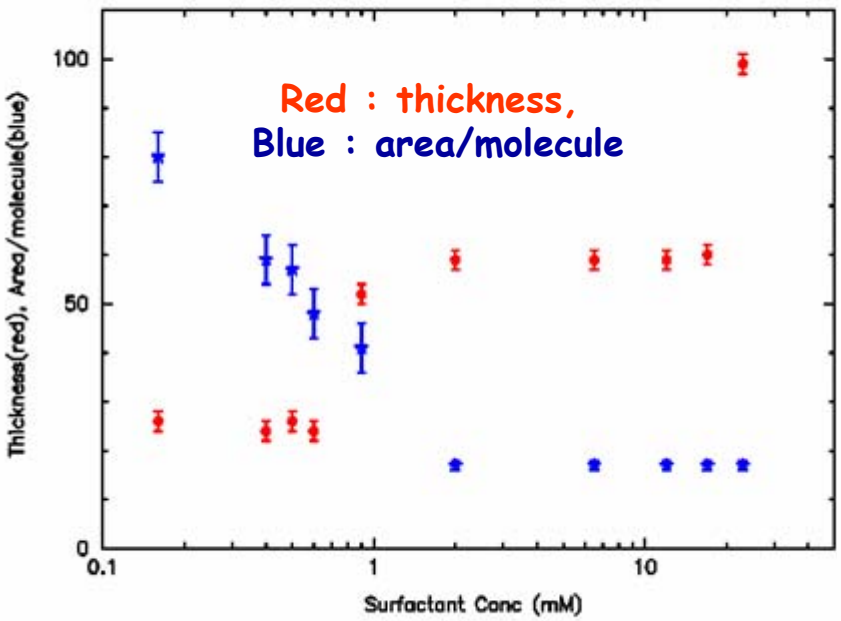


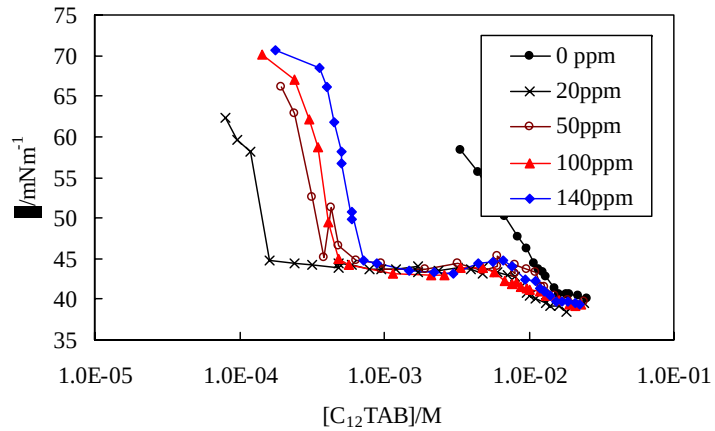


With increasing temp
see increased order,
decrease in spacing,
and increasing in-plane
correlation length

Off-specular, arising from conformal roughness,
analysed to obtain in-plane correlation length
~ 10 to 60 microns

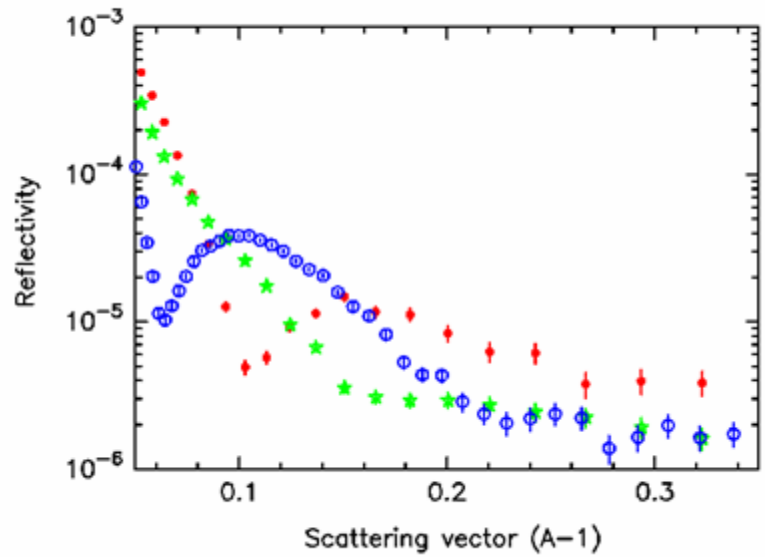
NaPSS(140ppm)/C12TAB





140 ppm polymer

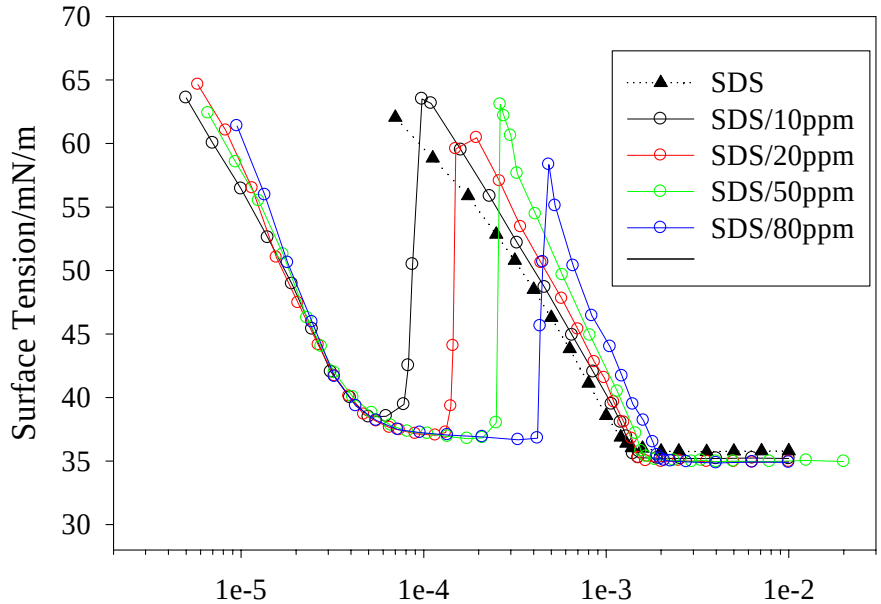
At low surf concs, monolayer ~20Å
20% vol fraction polymer.
At higher surf concs see more ordered structure, 'layering' of polymer/surfactant complexes



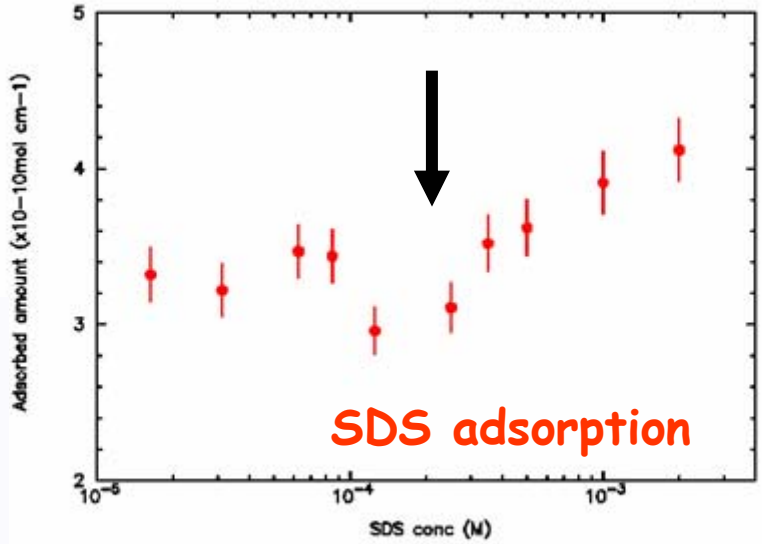
1.2 x 10-2M C12TAB
Red : dC12TAB/hNaPSS/cma
Blue : hC12TAB/hNaPSS/D2O
Green : dC12TAB/hNaPSS/D2O

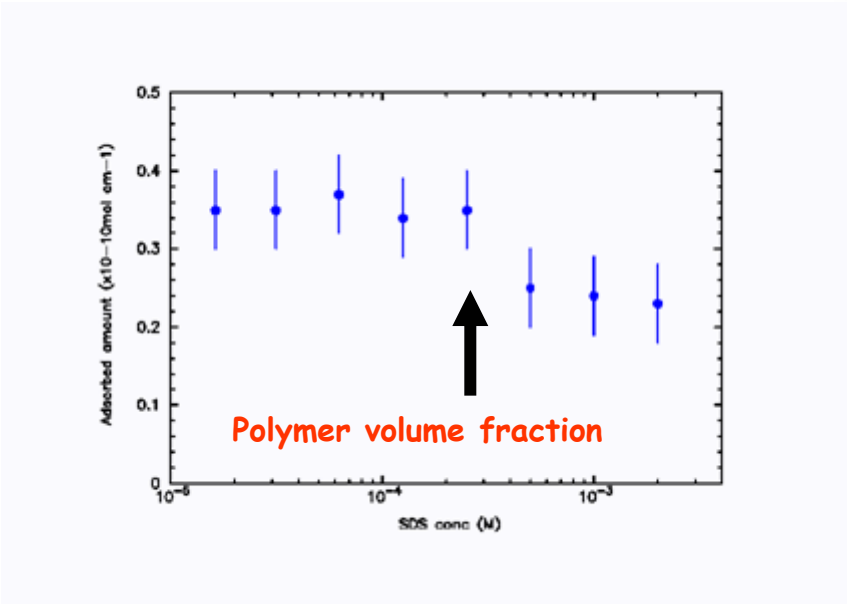
(Taylor, Thomas, Penfold, Langmuir 18 (2002) 4748,
Taylor, Thomas, Li, Penfold, Langmuir 19 2003 3712,
Taylor, Thomas, Hines, Humphreys, Penfold, Langmuir 2003)

SDS / poly-dmdaac / 0.1M NaCl



Mixed monolayer formed, ~ 20-25 Å, variation in SDS and polymer adsorption

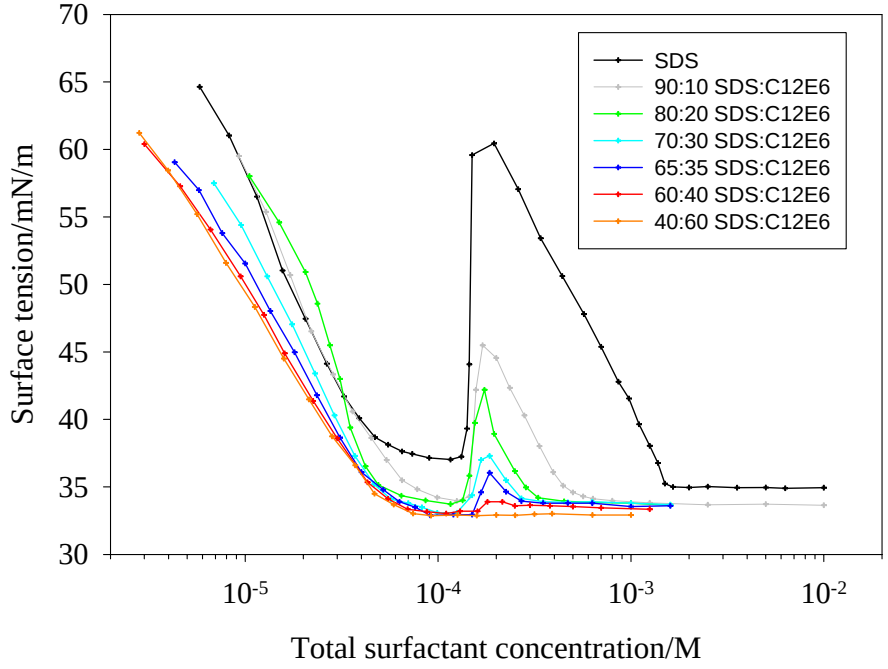


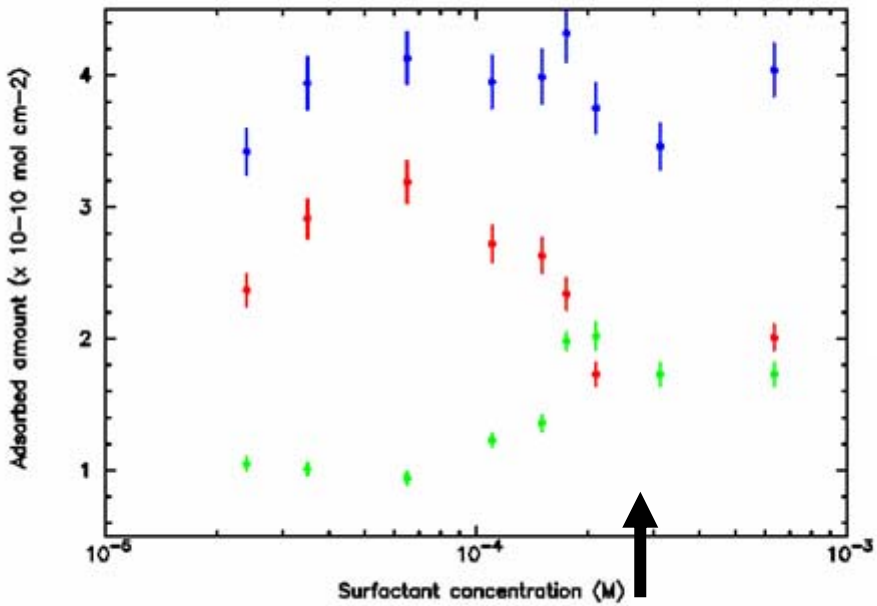


SDS / 10 ppm poly-dmdaac / 0.1 M NaCl

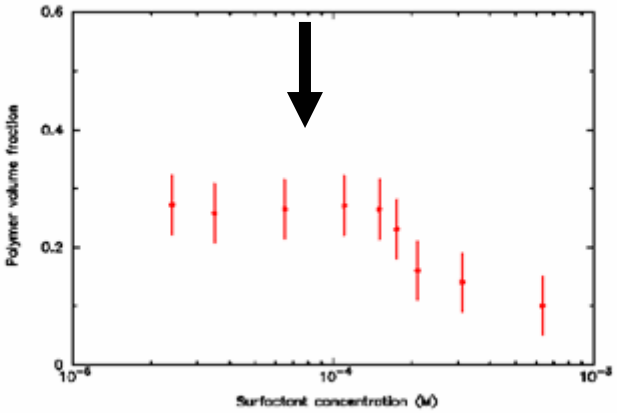
(Staples, Tucker, Penfold, Warren, Thomas, Langmuir 2002 18 5139)

SDS / C12E6 / 20ppm poly-dmdaac / 0.1M NaCl





Adsorbed amount of surfactant
Blue : total, red : SDS,
green : C12E6



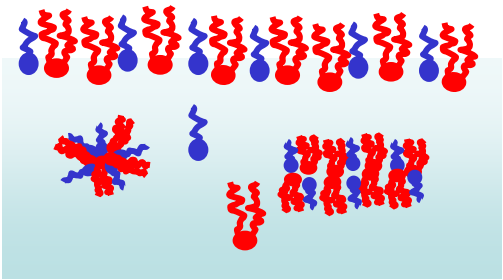
Polymer volume fraction

80/20 SDS / C12E6/ 20ppm poly-dmdaac / 0.1 M NaCl

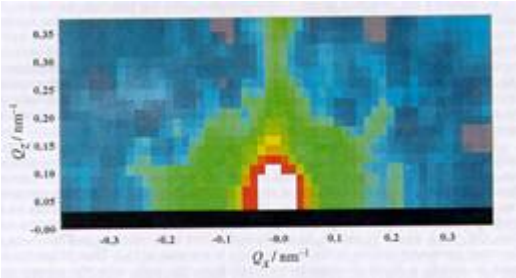
(Staples, Tucker, Penfold, Warren, Thomas, Taylor, Langmuir 2002 18 5147)

Future Prospects

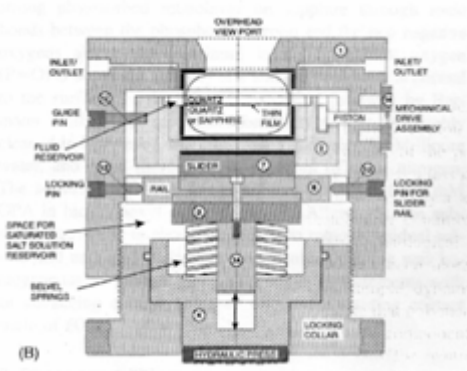
- **Surface in equilibrium with complex bulk solution**



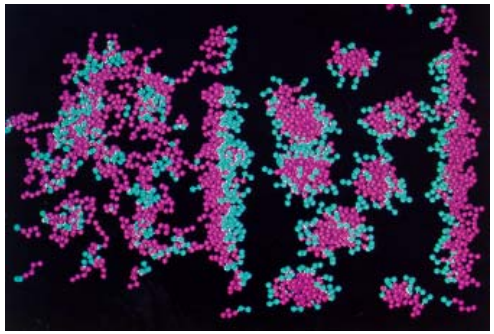
Simultaneous Reflectivity and SANS



- **Surface Ordering**

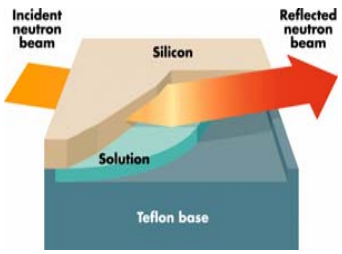


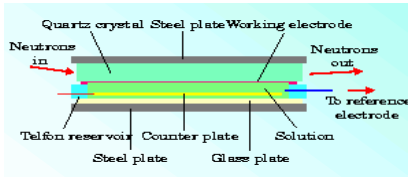
Due to interface, confinement, flow



Future Prospects

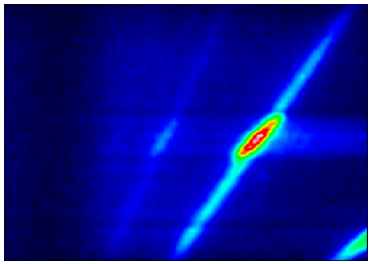
- **Liquid-solid, liquid-liquid interfaces**

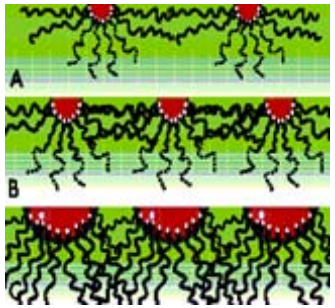




Broader range of interfaces and conditions accessible

- **Lateral structure**

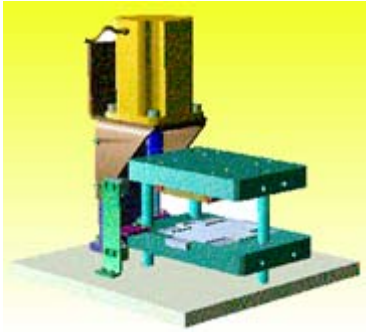




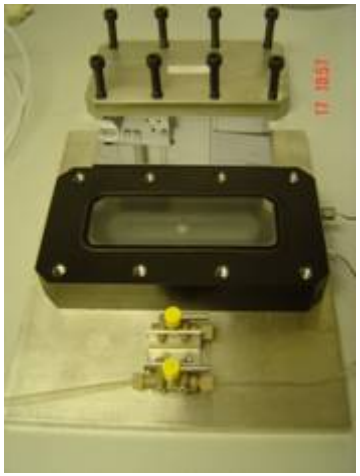
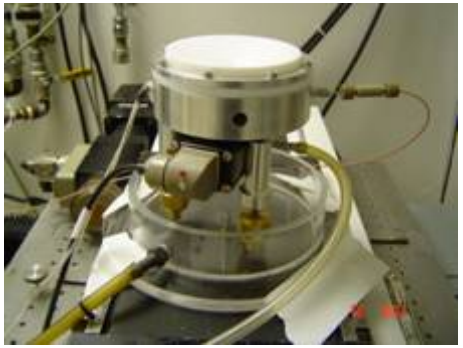
Surface inhomogeneities, surface micellisation, segregation

- **Non-equilibrium effects**

Kinetics of absorption, dynamic surface tension, Surface rearrangements



Future Prospects

- **High Throughput**

Multi-component mixtures,
parameter space