放射光を利用したソフト界面膜の構造解析

Structure Analysis of Soft Interfaces by Synchrotron Radiation

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Purpose

Application of X-ray reflection to Liq./Liq. Interface on the basis of thermodynamic information to draw precise picture of Gibbs adsorbed films

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INTRODUCTION

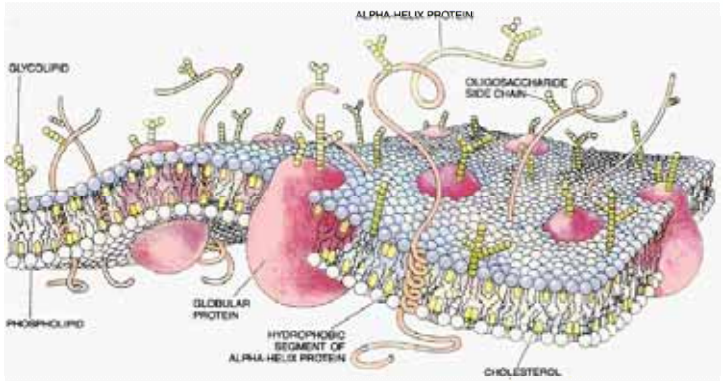
Interface ; thickness with nm order (nanospace)

Soft interface
(Gas/Liq., **Liq./Liq.**) → fundamental structure of complicated molecular organized systems

Recent progress on X-ray reflection at Liq./Liq. interface

↓

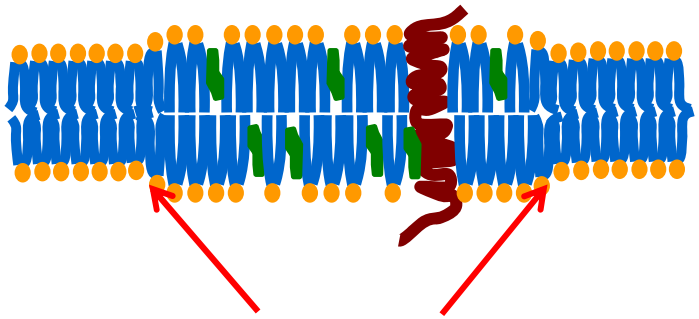
Structure analysis of Liq./Liq. interface



(Bretscher, Scientific American 1985)

→

Biomembrane **Raft**



domain boundary (line)

CONTENTS

X-ray reflection (XR)

- Adsorption of **FC, HC alcohols** at hexane/water interface

  structure of condensed FC and HC alcohol films

  domain formation of FC alcohol

- **Adsorption of FCdiol** at hexane/water and air/water interfaces

  spontaneous multilayer formation

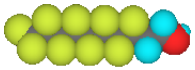
Total reflection XAFS

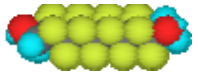
- **Adsorbed film of cationic surfactant** at hexane/water interface

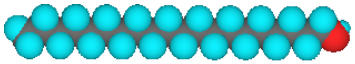
  staggered arrangement of surfactant ions

EXPERIMENTAL

Materials:

Perfluorodecanol (**FC10OH**) $CF_3(CF_2)_7(CH_2)_2OH$ 

Perfluorodecane-1,10-diol (**FC10diol**) $HOCH_2(CF_2)_8CH_2OH$ 

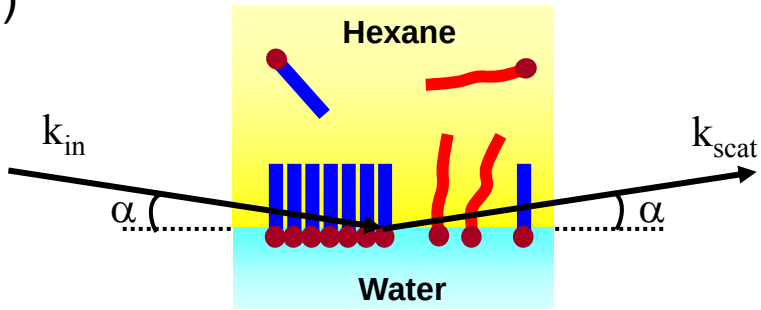
1-Icosanol (**C20OH**) $CH_3(CH_2)_{19}OH$ 

Measurements:

Interfacial tension

Pendant drop method (± 0.05 mN m^{-1})

Temperature ***T***
Pressure ***p***
Molality ***m***

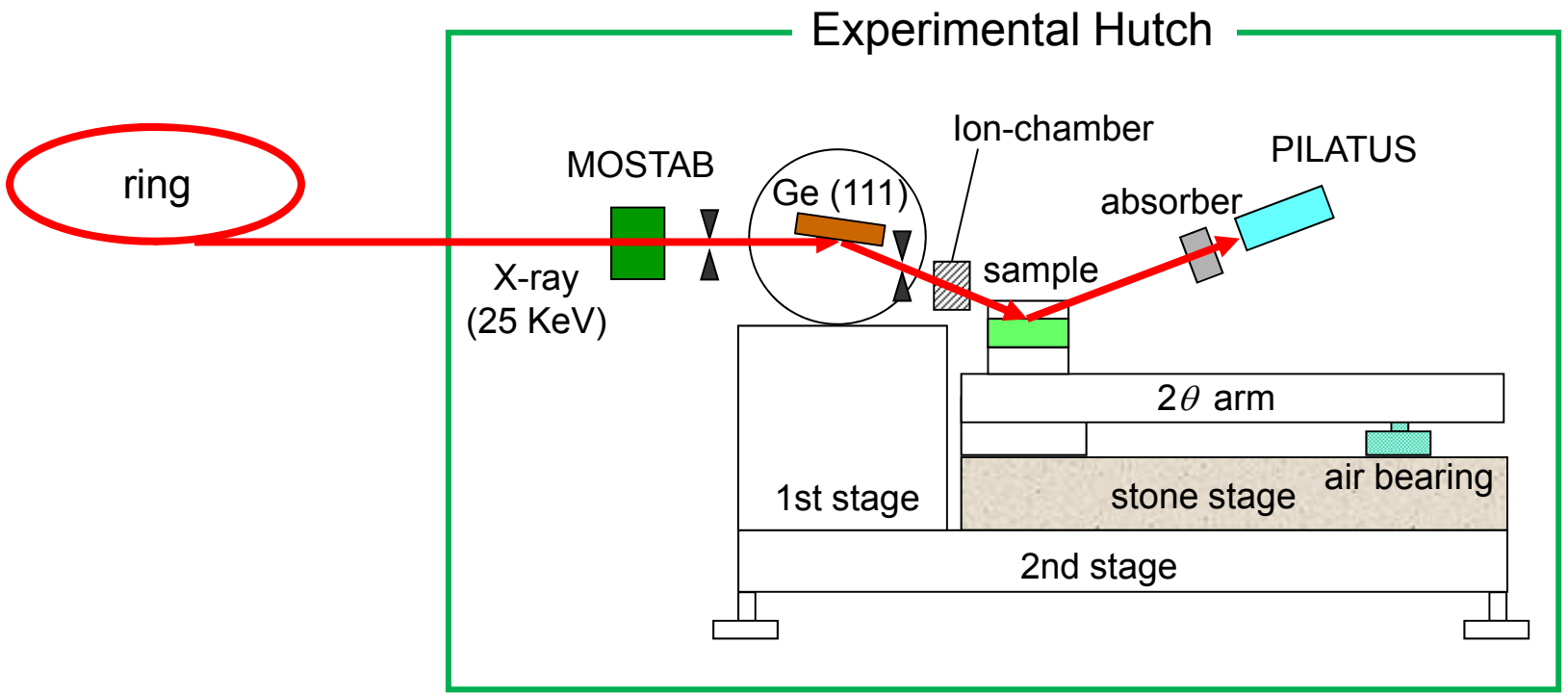


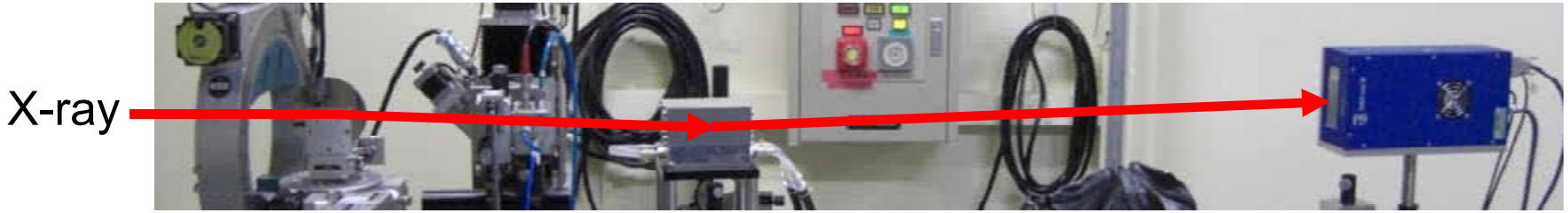
X-ray reflectivity

APS in ANL Sector 15 (λ = 0.4119 Å)
SPring-8 BL37XU (λ = 0.4959 Å)

Temperature ***T***
Scattering vector $\mathbf{Q_z}$ (= $(4\pi/\lambda)\sin\alpha$, α : incident angle)

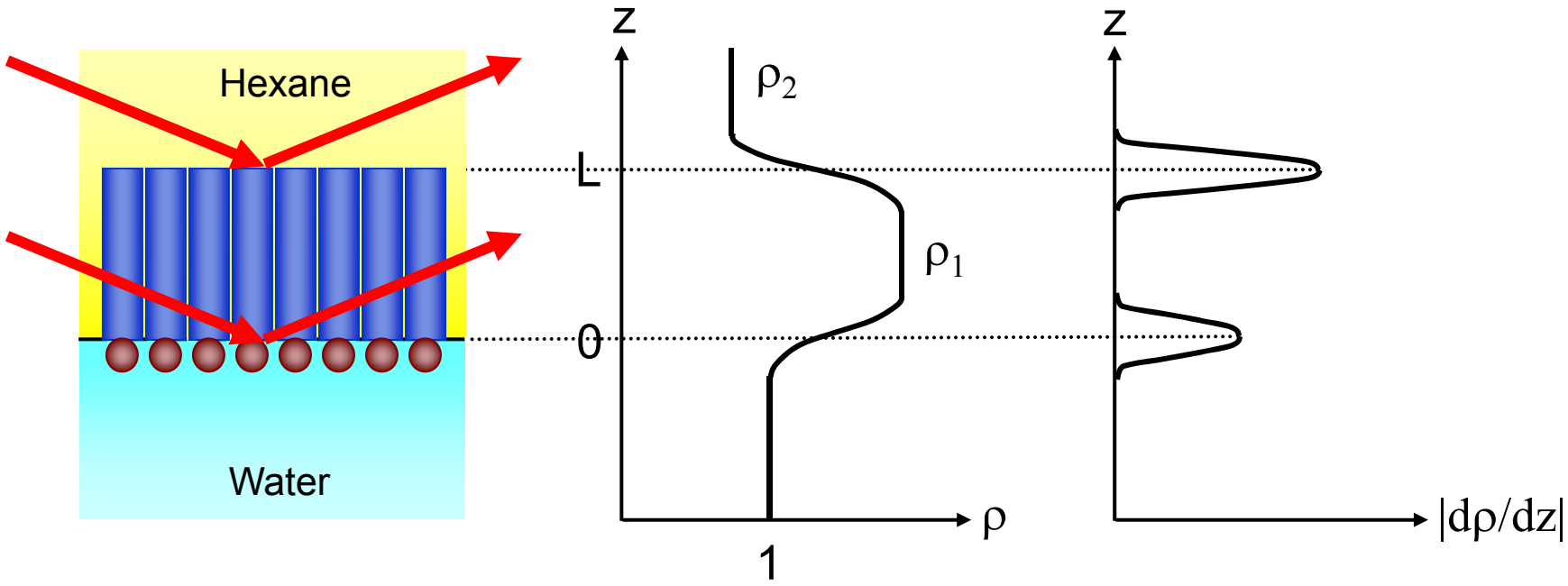
XR SPECTROMETER AT BL37XU IN SPring-8

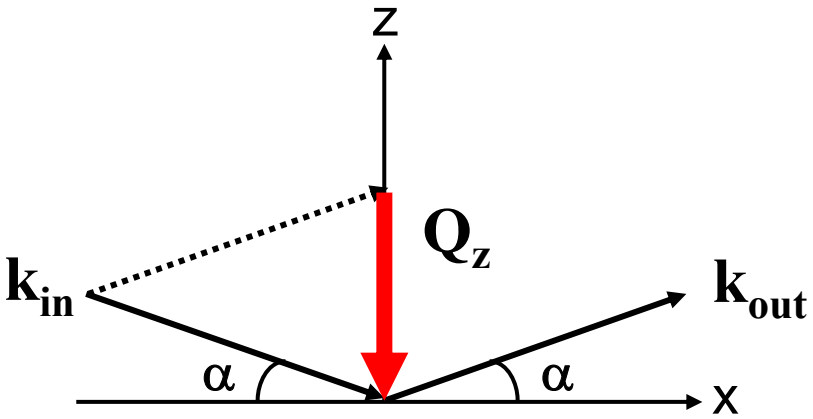




Ge(111) sample cell PILATUS

PRINCIPLE OF X-RAY REFLECTION





$$\mathbf{Q_z = k_{out} - k_{in}} = (4\pi/\lambda)\sin\alpha$$

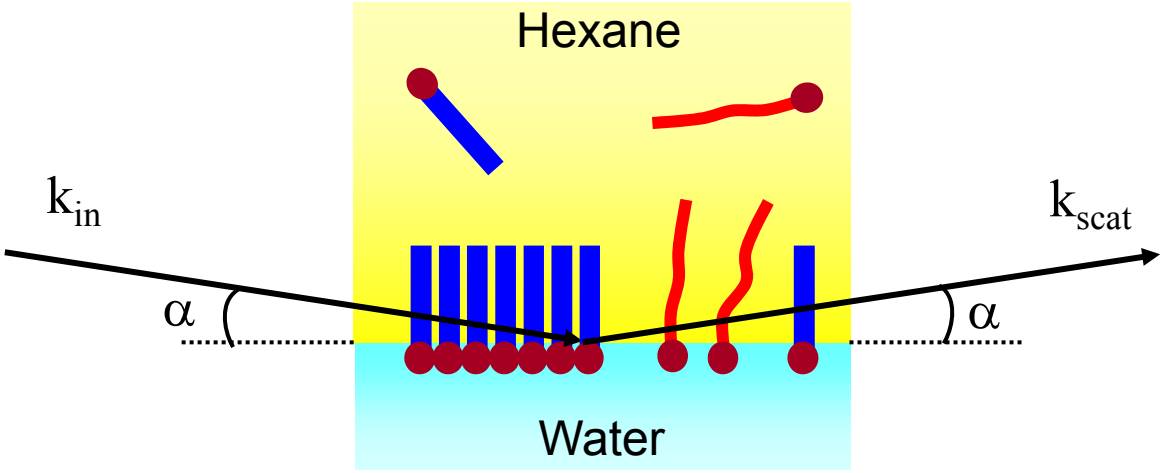
$$\frac{R(Q_z)}{R_F(Q_z)} \cong \left| \frac{1}{\Delta\rho} \int dz \frac{d\langle\rho(z)\rangle}{dz} \exp(iQ_z z) \right|^2$$

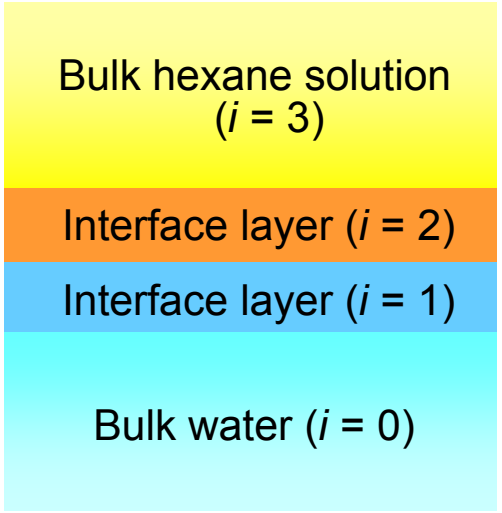
$$\rho(z) = \frac{1}{2}(1-\rho_1)[1+\mathrm{erf}(z/\sqrt{2}\sigma)] + \frac{1}{2}(\rho_1-\rho_2)\{1+\mathrm{erf}[(z-L)/\sqrt{2}\sigma]\} + \rho_2$$

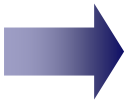
$$\rho_1 = \rho_{FC}/\rho_w \qquad \rho_2 = \rho_h/\rho_w$$

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2)dt$$

DATA ANALYSIS







Layer thickness : *L*

Electron density : $\rho(z)$

Roughness : σ

Coverage : *C*

Layer model for a monolayer at hexane/water interface

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Total reflection XAFS

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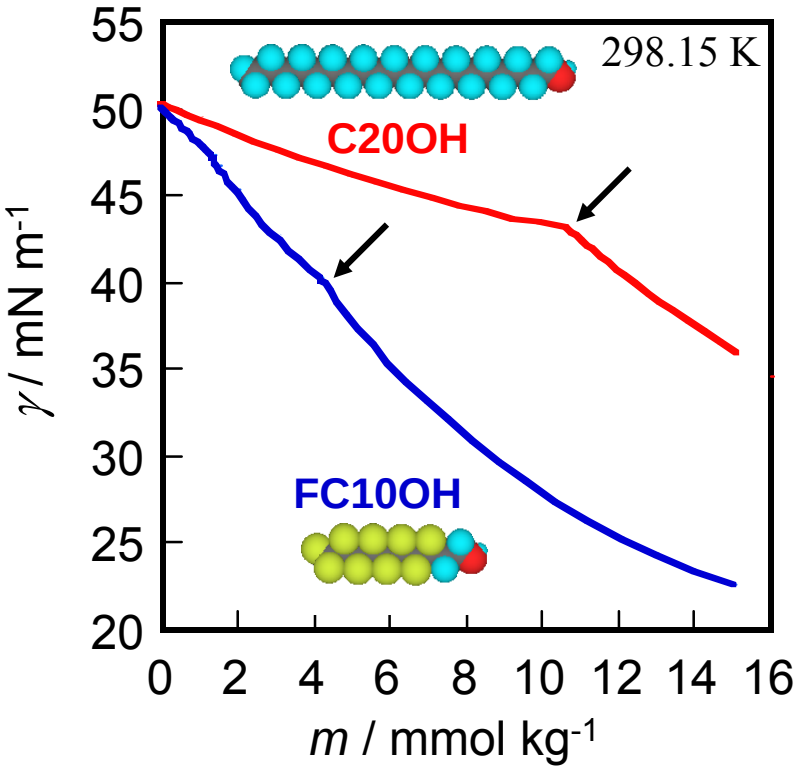
  staggered arrangement of surfactant ions

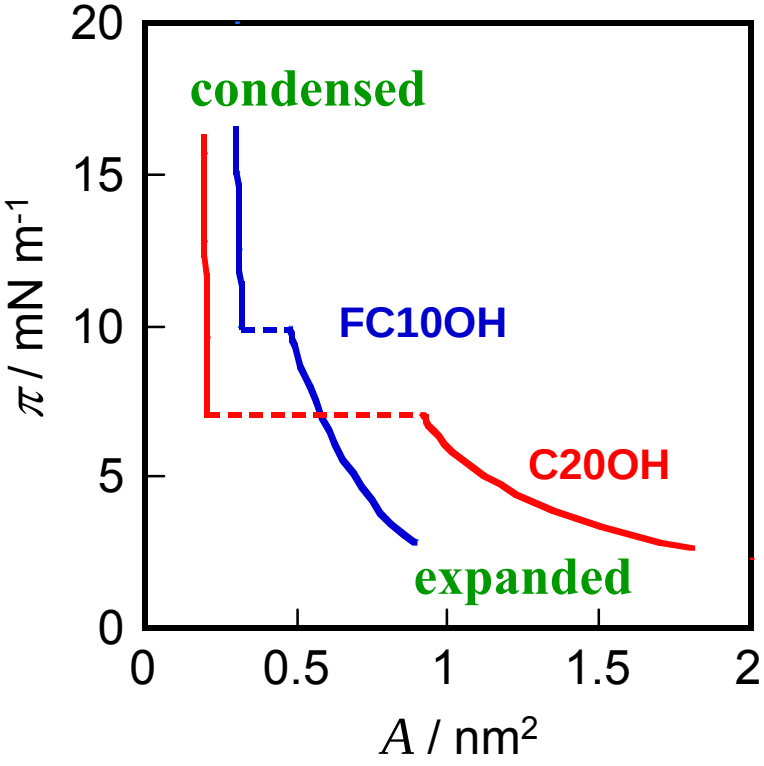
THERMODYNAMIC DATA (C20OH & FC10OH at C6/WATER INTERFACE)

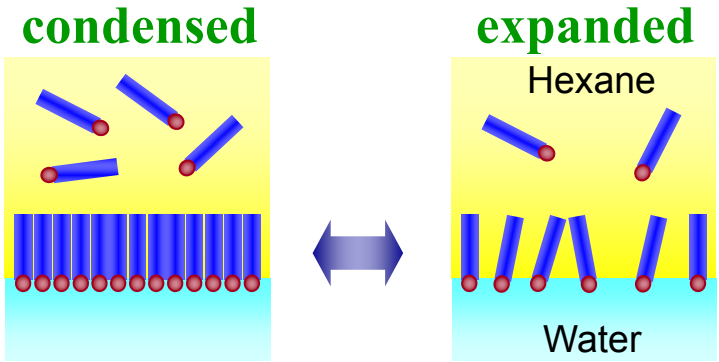
Interfacial tension vs. concentration



break point ➡ phase transition

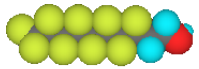
Interfacial pressure vs. area per molecule

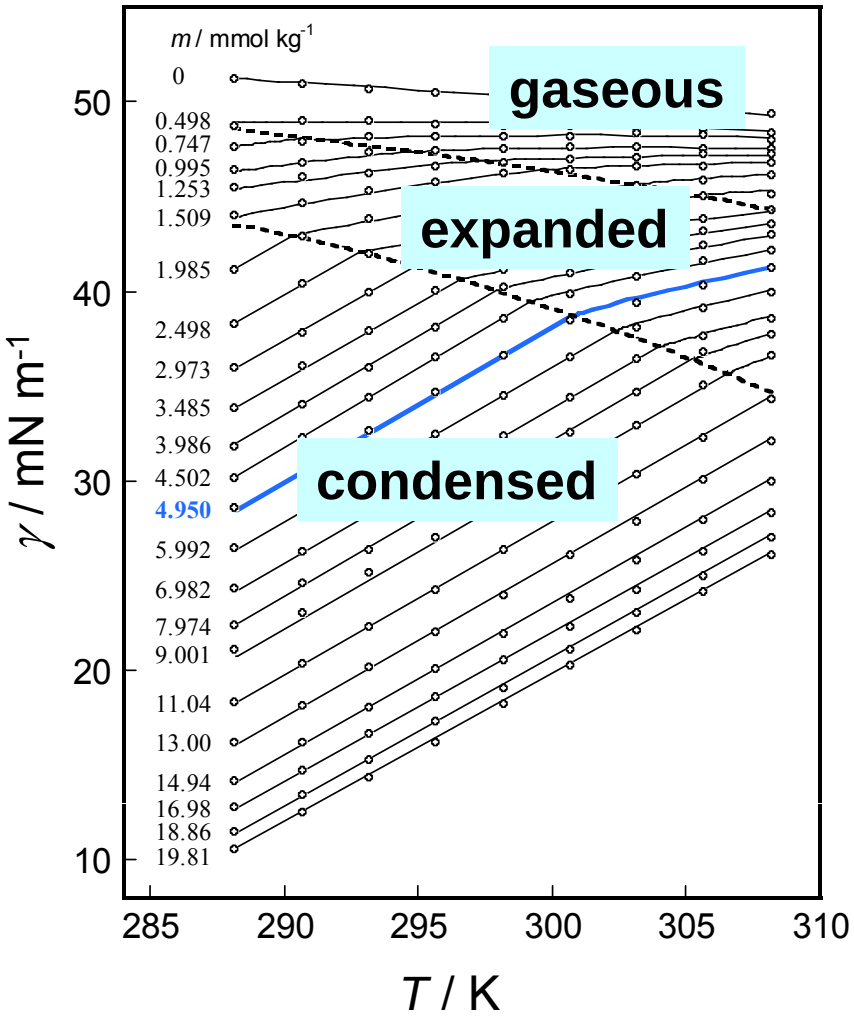




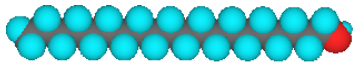
INTERFACIAL TENSION (PURE TFC10OH & C20OH)

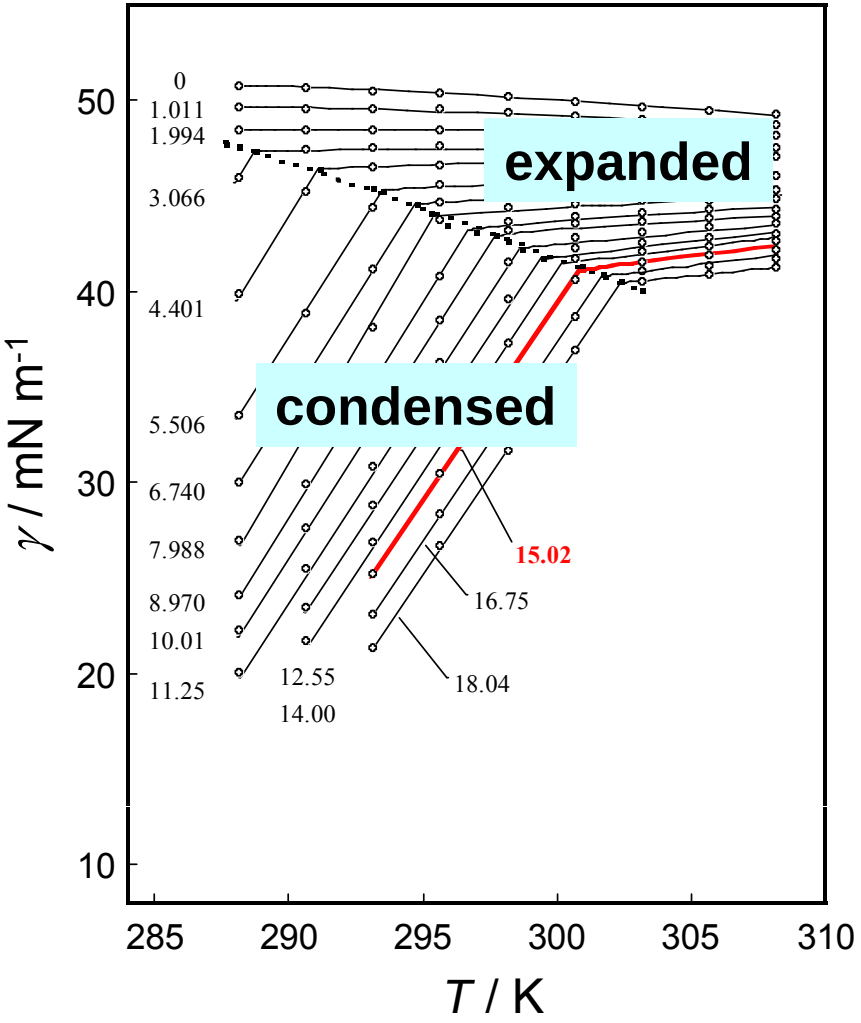
FC10OH





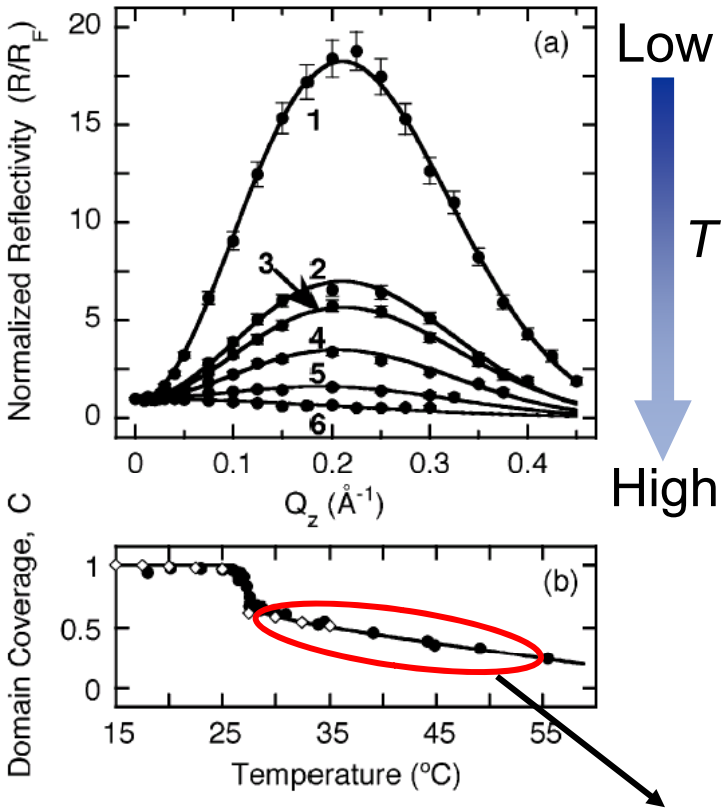
C20OH

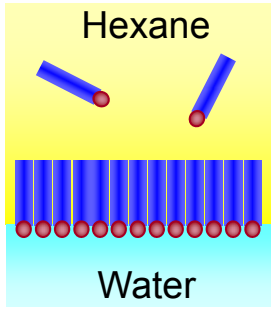




REFLECTIVITY (FC10OH & C20OH at C6/WATER INTERFACE)

FC10OH (m_1 = 5 mmol kg^{-1})

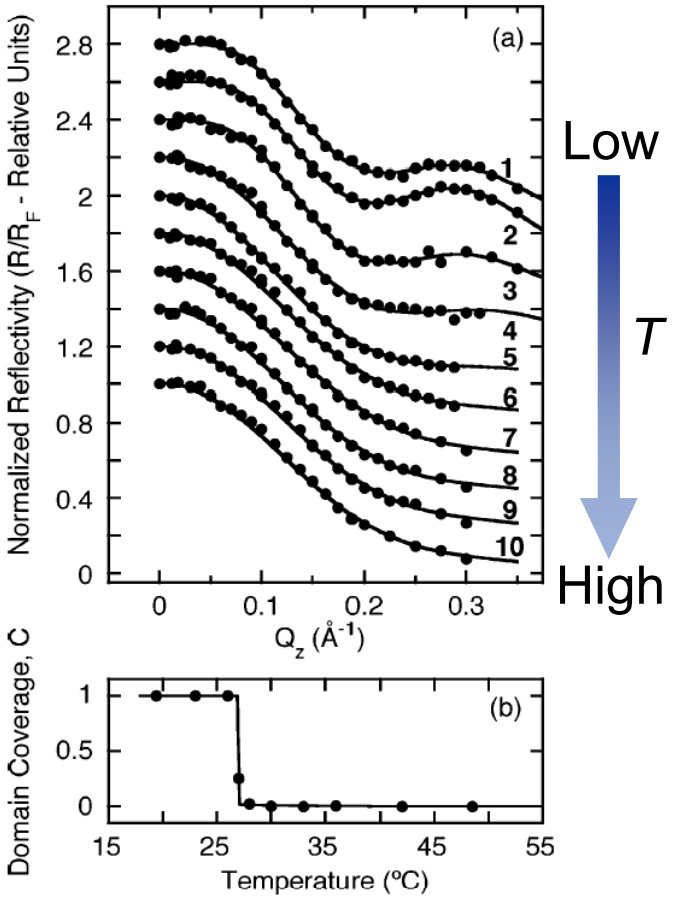


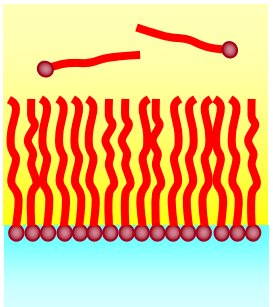


$\rho / \rho_w = 1.85^{\pm 0.09}$

2D solid

C20OH (m_1 = 15 mmol kg^{-1})

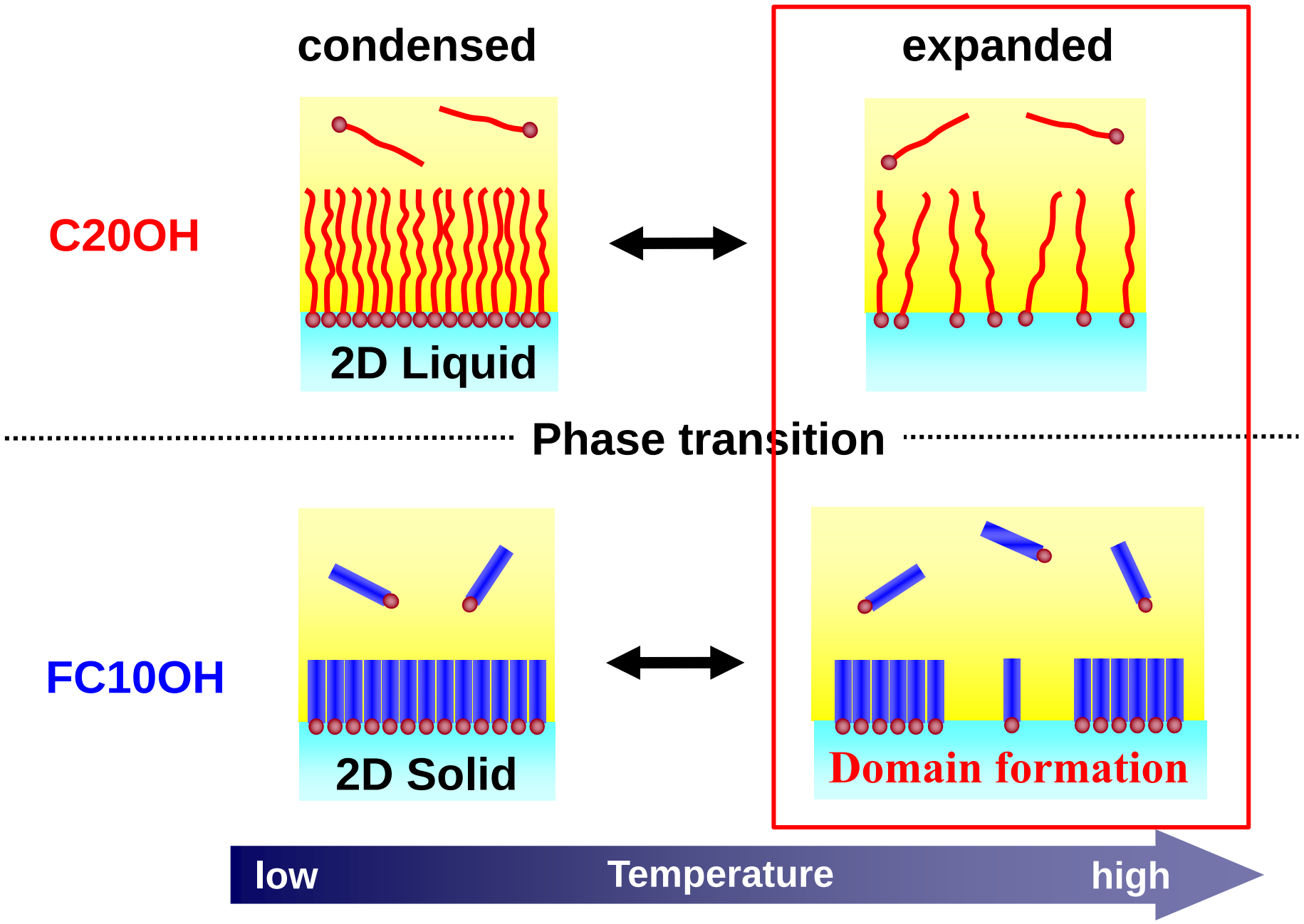




$\rho / \rho_w = 0.80^{\pm 0.02}$

2D liquid just above freezing point

SEQUENCE OF ADSORBED FILM



DOMAIN FORMATION OF FC10OH

Excess Gibbs Energy of Mixing

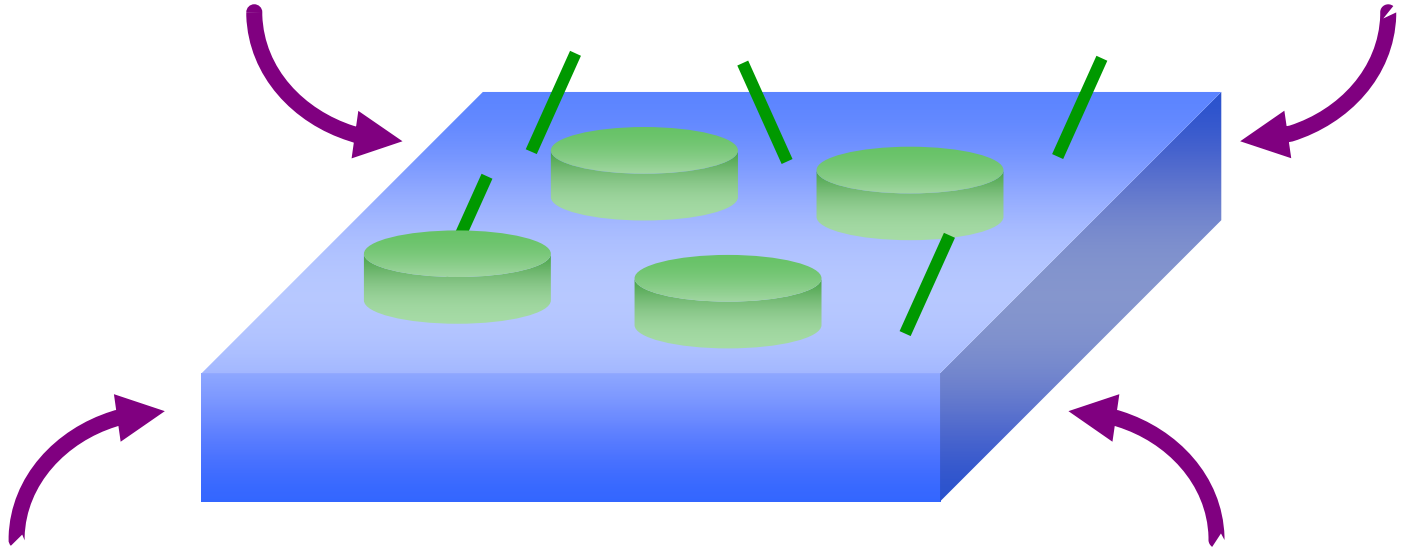
Alcohol + Hexane at interface

molecular dispersion or aggregation

Domain Line Tension

domain / surrounding boundary

shrink domain boundary



Interaction between Domains

VDW interaction

stability against cohesion of domains

Dipole - Dipole Interaction

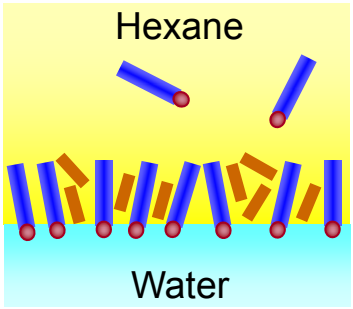
interfacial density in domain

expand domain boundary

DOMAIN FORMATION OF FC10OH

Excess Gibbs Energy of mixing

Hexane + Perfluorohexane ; $g^E \backsim$ **1.3 kJ mol^{-1}**



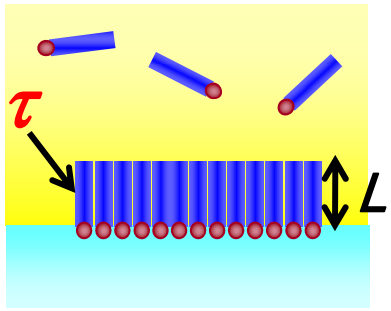
FC10OH domain formation (not for molecular dispersion)

Domain Line Tension ; $\tau \approx \gamma L$

FC10/C6 interface : $\gamma = \gamma_{C6} + \gamma_{FC10} - 2(\gamma_{C6}\gamma_{FC10})^{1/2} = 1.5$ mN m^{-1}

C20/C6 interface : $\gamma \approx 0$ mN m^{-1}

contact height : L = 1.3 nm (FC domain)



FC10OH : $\tau \sim$ 2 pN **C20OH : $\tau \sim$ 0 pN**

FC10OH : large domain formation

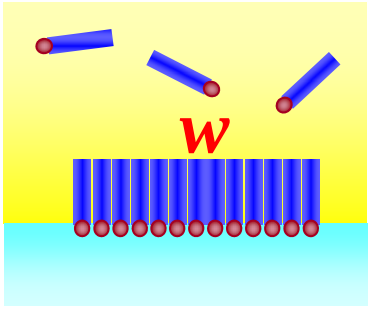
C20OH : molecular dispersion

DOMAIN FORMATION OF FC10OH

- **Dipole – Dipole Interaction** : $w = (u^2/4\pi\varepsilon_0\varepsilon)ln(4R/e^2\Delta)$

  Interfacial density : FC10OH < C20OH

  more repulsive for C20OH than for FC10OH



FC10OH : large domain formation

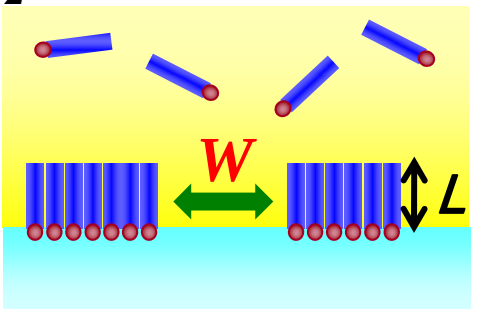
C20OH : molecular dispersion

- **Interaction between Domains** : $W = -ALR^{1/2}/24D^{3/2}$

  Hamaker const. : A = 2.75 x 10^{-21} J (FC10OH)

  A = 3.74 x 10^{-21} J (C20OH)

  $W_{FC10} > W_{C20}$: **more attractive for C20OH**



FC10OH domains are more stable against cohesion

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Total reflection XAFS

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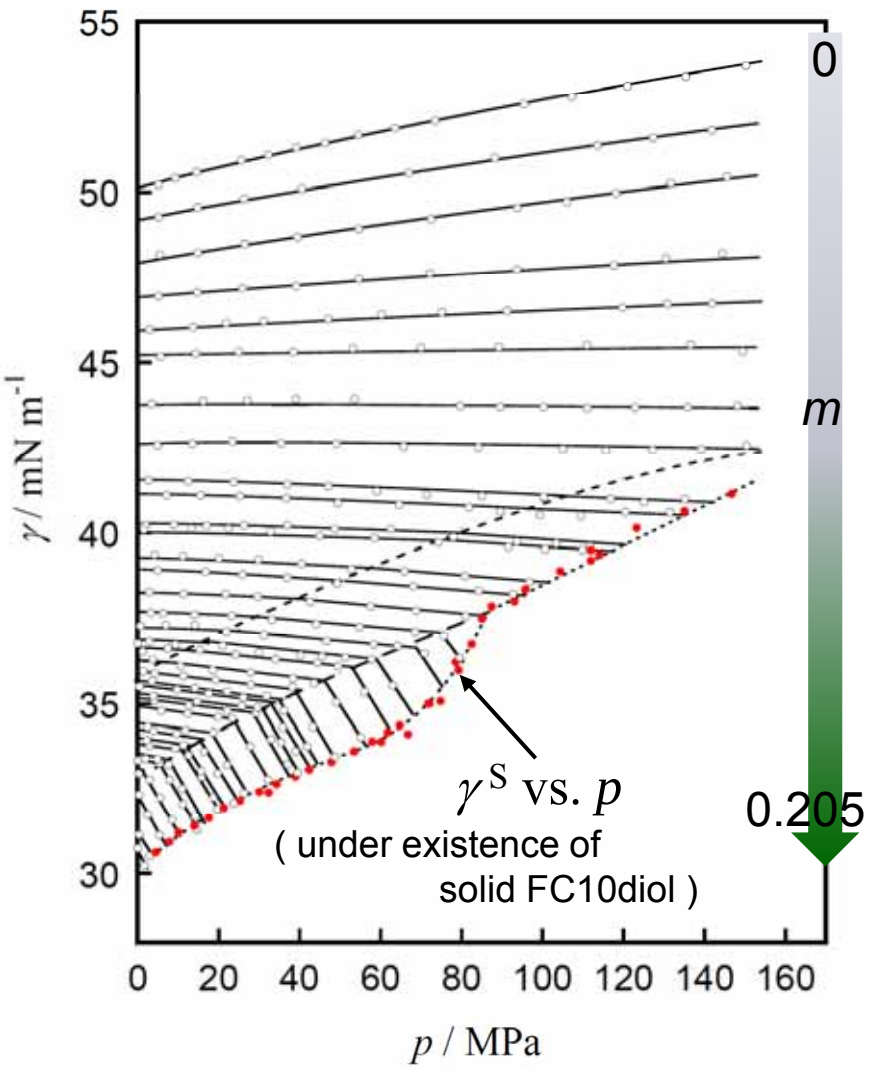
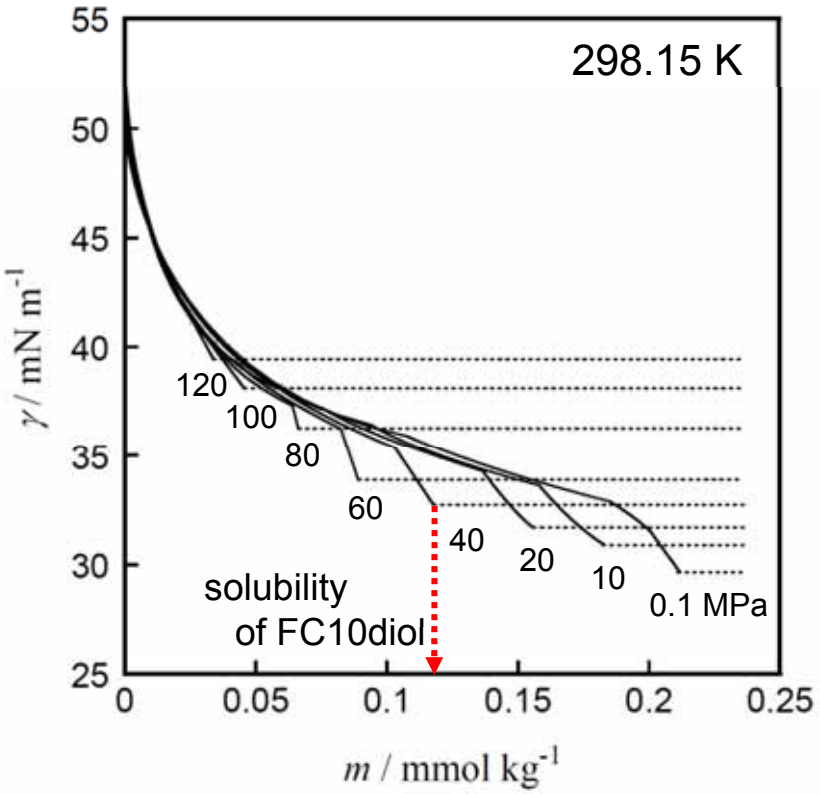
INTERFACIAL TENSION (FC10diol)

Interfacial tension vs. pressure



Interfacial tension vs. molality

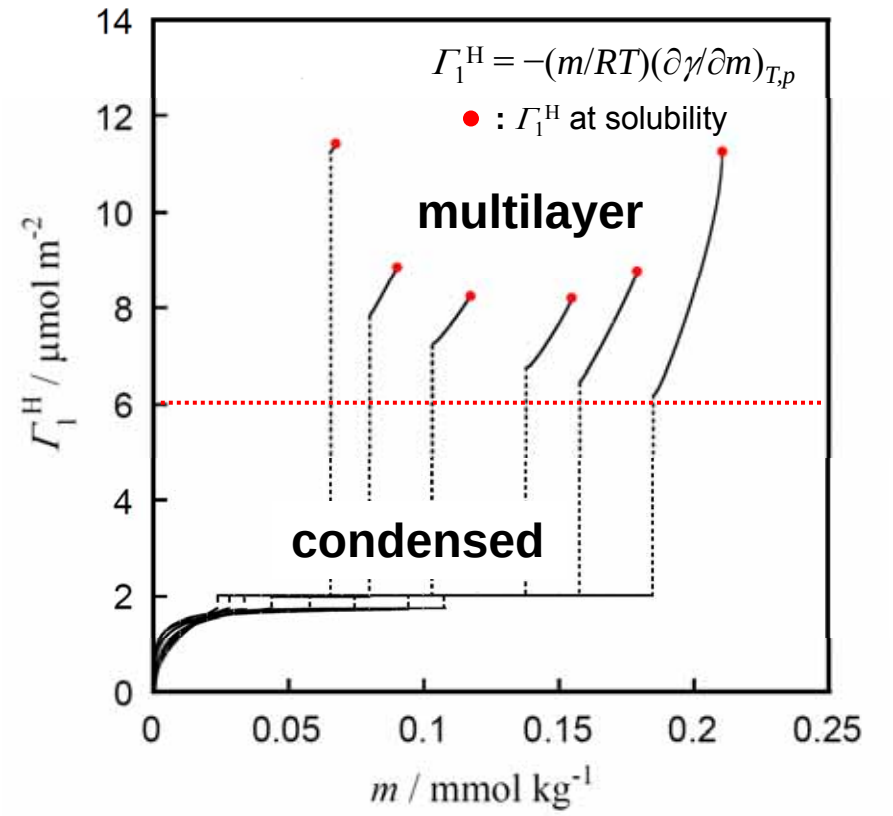


break points at high concentration & high pressure

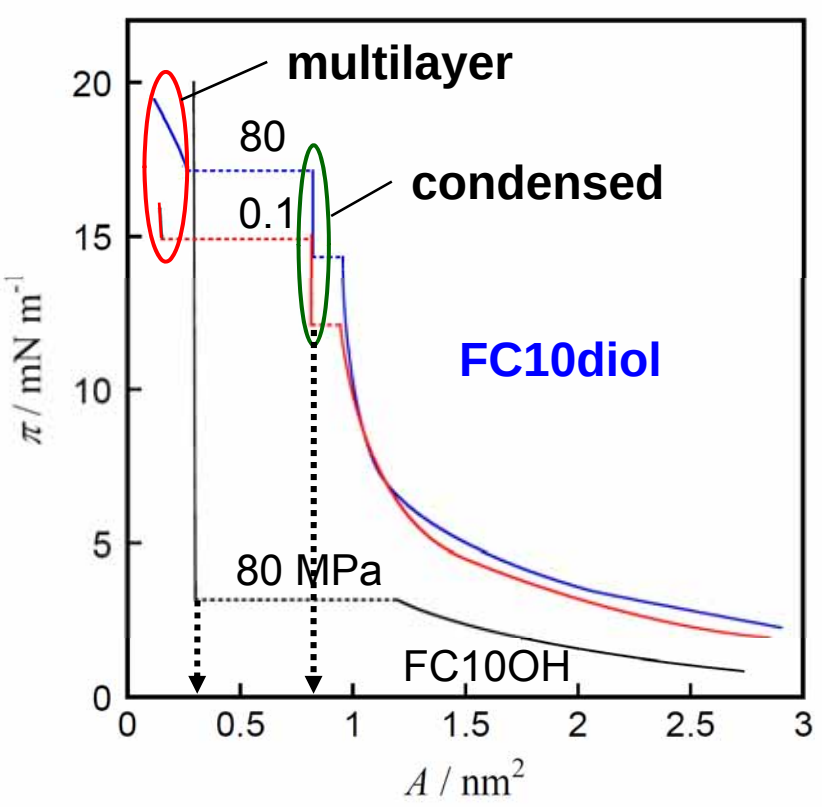
phase transitions in adsorbed film

STATE OF ADSORBED FILM (FC10diol)

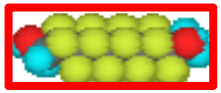
Interfacial density vs. molality



Interfacial pressure vs. area per molecule



condensed film with parallel orientation



0.85 nm^2

spontaneous formation of multilayer

0.28 nm^2

PARTIAL MOLAR VOLUME IN MULTILAYER

Partial molar volume of FC10diol at 0.1 MPa

state	m (mmol kg^{-1})	Γ_1^H (μmol m^{-2})	$\bar{v}_1^H$ (cm^3 mol^{-1})
multilayer	0.185	6.19 (small)	**224**
	0.195	7.87	232
	0.205	10.20 (large)	238
condensed monolayer	0.185	2.04	254
solid	0.209	11.21	*224

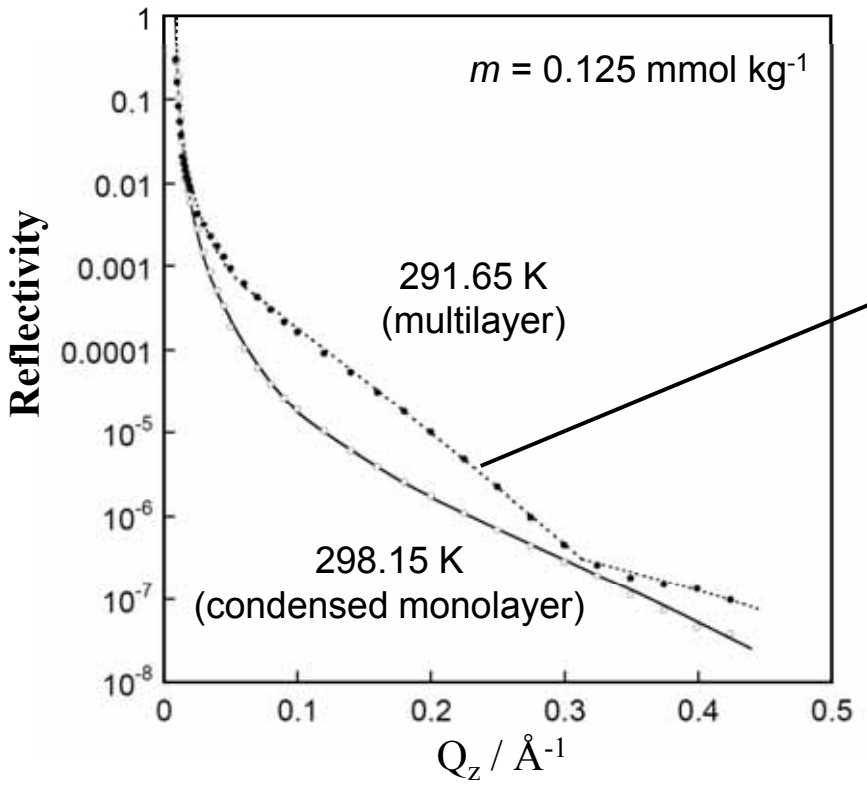
* molar volume of solid FC10diol ; v_1^S

$v_1^{H,M}$ is almost equal to v_1^S just above phase transition point.

v_1^H increases with molecular piling.

→ structure analysis by XR

X-RAY REFLECTIVITY



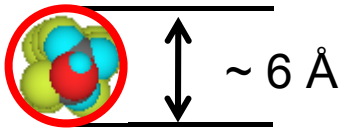
oscillation with short period

⬇

thicker layer formation

Layer thickness and electron density of adsorbed film

system	state		L / Å	ρ/ρ_w
FC10diol	condensed (parallel)		5.23 ± 1	1.40 ± 0.1
	multilayer	Layer 1	15.5 ± 2	1.68 ± 0.2
		Layer 2	14.6 ± 2	1.44 ± 0.3
FC10OH	condensed (normal)		10.0 ± 1	1.85 ± 0.09

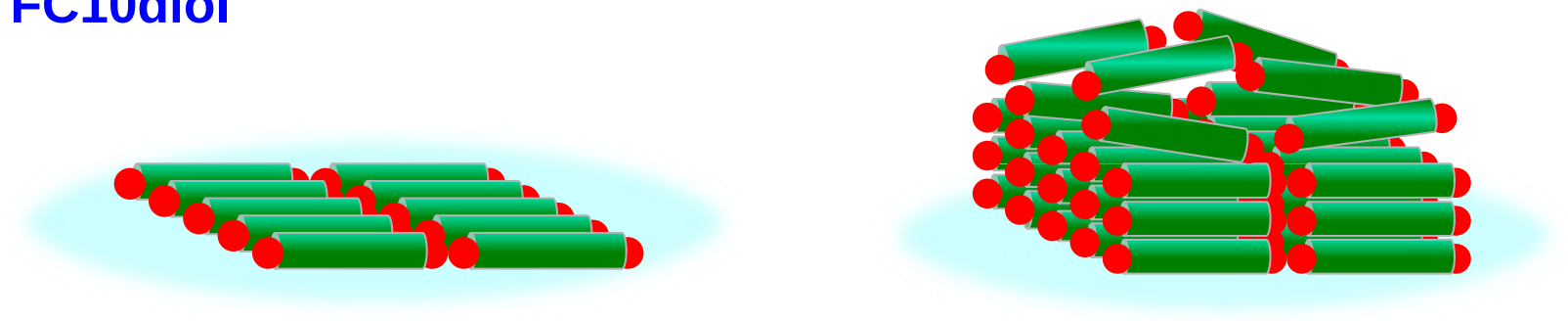


parallel orientation

dense packing in lower layer
loose packing in upper layer

ILLUSTRATION OF ADSORBED FC10diol FILM

FC10diol

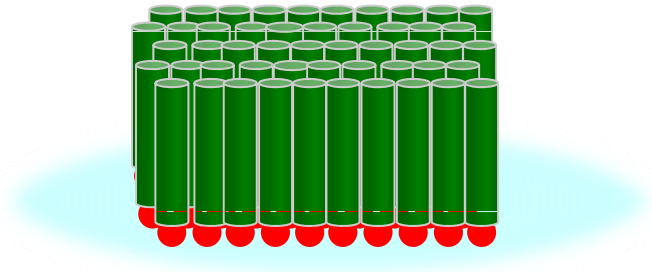


parallel condensed monolayer **multilayer**

Multilayer is not simply formed by piling the condensed monolayer.

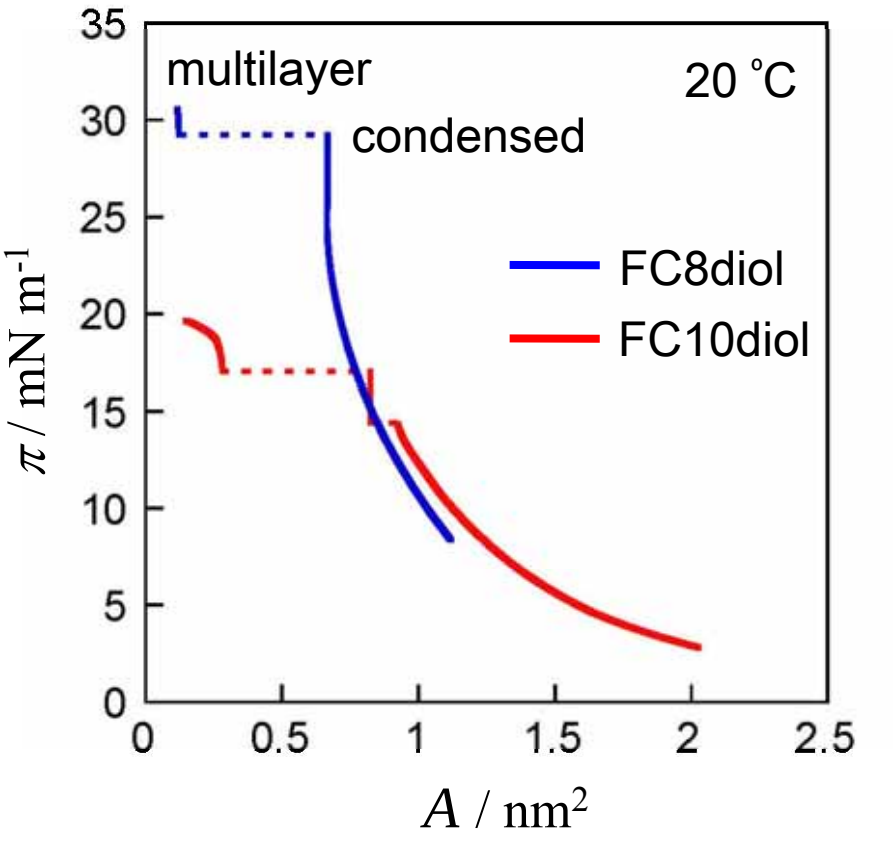
Molecular packing is looser in the upper layer than in the lower layer.

FC10OH

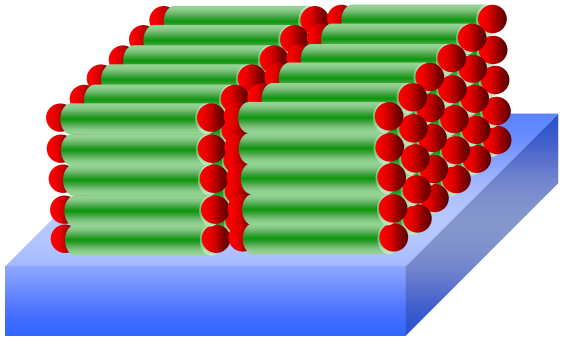


perpendicular condensed monolayer

MULTILAYER FORMATION (C6/Water vs. Air/Water)

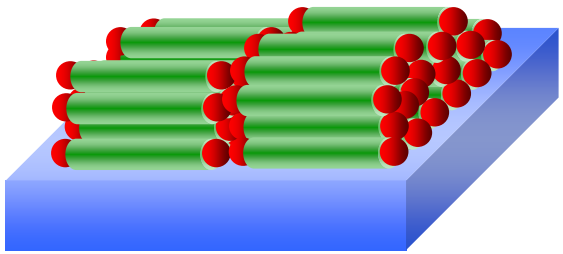


FC8diol
at air / water interface



dense packing at air/water interface

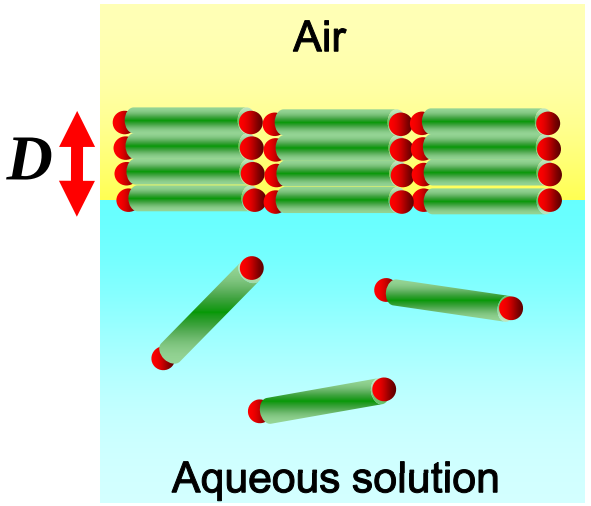
FC10diol
at hexane / water interface



MULTILAYER FORMATION (SURFACE FORCE)

Surface forces between the upper and lower interfaces

$$W = -\frac{A}{12\pi D^2}$$



A : Hamaker constant

$$A = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu}{8\sqrt{2}}\frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}\{(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}\}}$$

FC8diol at Air / Water

$A = +1.67 \times 10^{-21}$ J

attractive

FC10diol at C6 / Water

$A = -2.54 \times 10^{-22}$ J

repulsive

CONTENTS

X-ray reflection (XR)

- Adsorption of **FC, HC alcohols** at hexane/water interface

  structure of condensed FC and HC alcohol films

  domain formation of FC alcohol

- **Adsorption of FCdiol** at hexane/water and air/water interfaces

  spontaneous multilayer formation

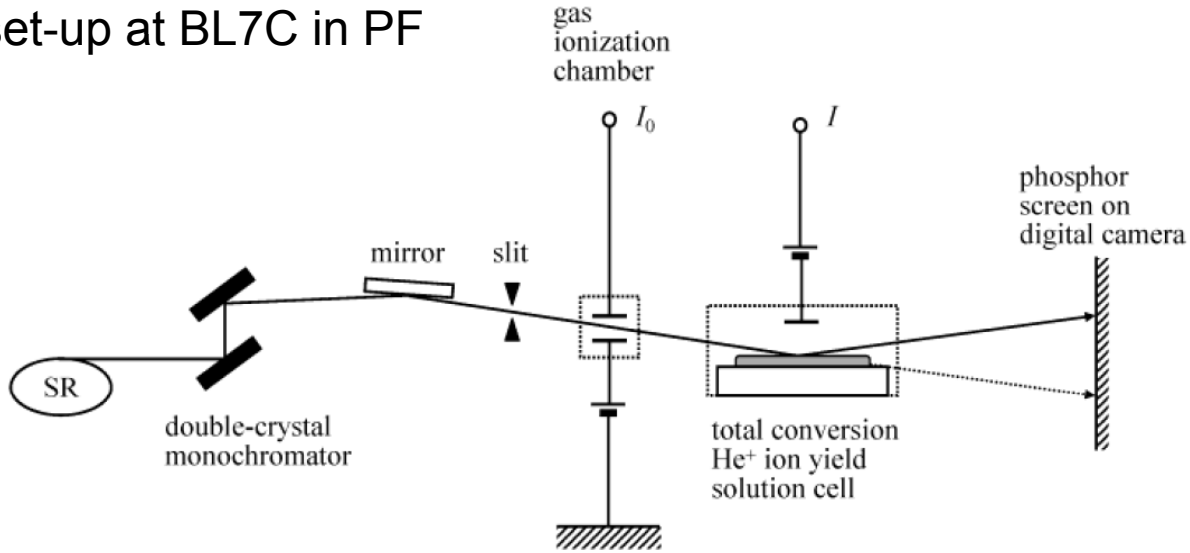
Total reflection XAFS

- **Adsorbed film of cationic surfactant** at hexane/water interface

  staggered arrangement of surfactant ions

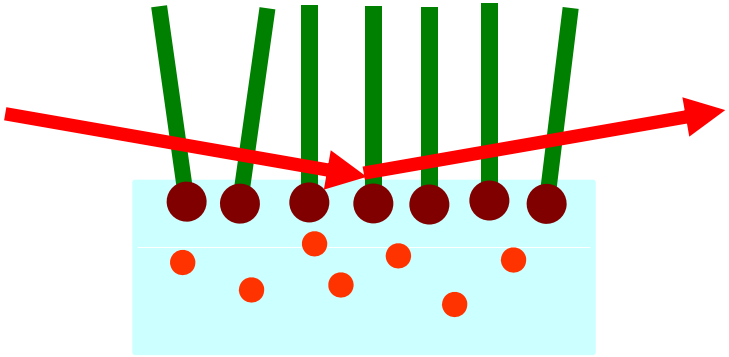
TOTAL-REFLECTION XAFS at AIR/WATER SURFACE

TR-XAFS set-up at BL7C in PF

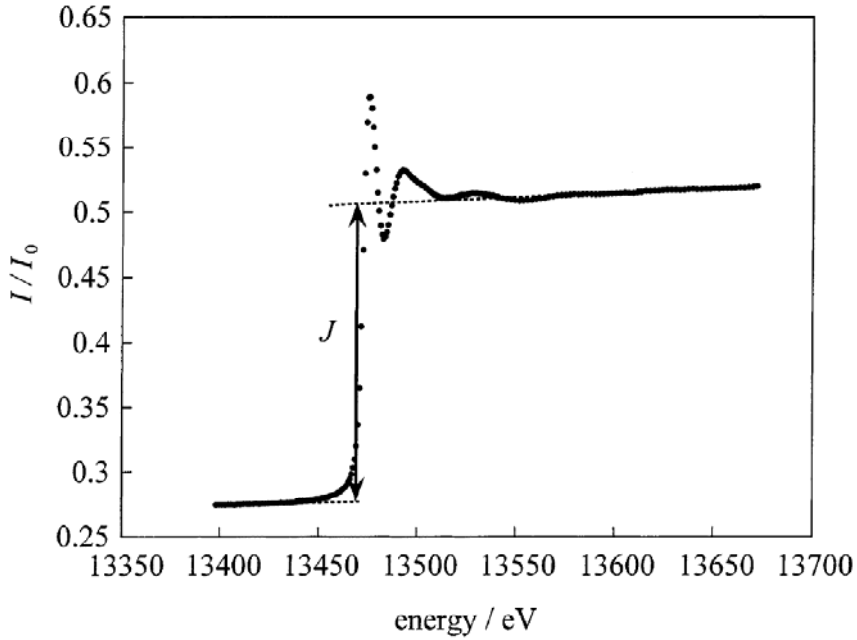


aqueous DTAB solution/air surface

$CH_3(CH_2)_{11}N^+(CH_3)_3\ Br^-$

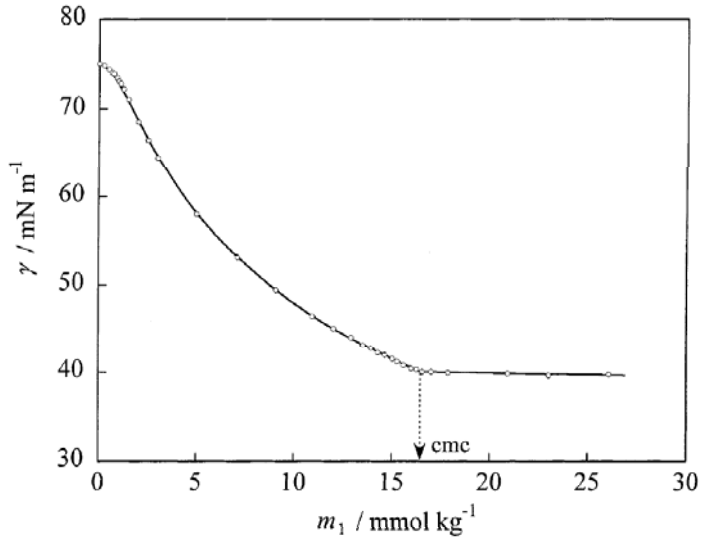


XAFS spectrum

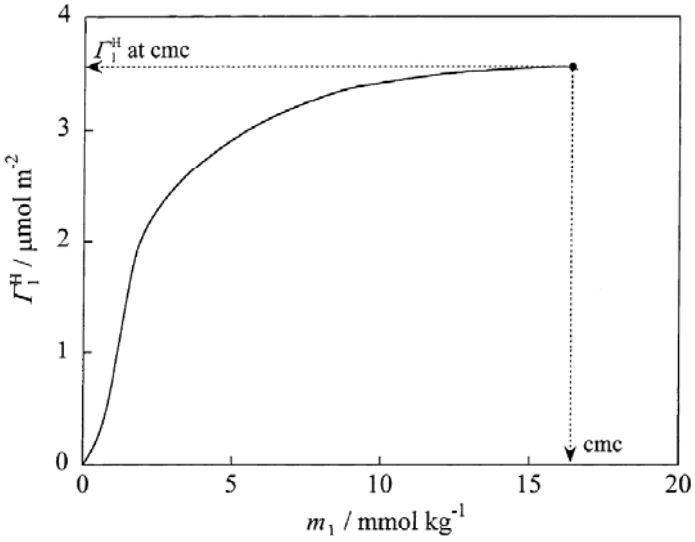


TOTAL-REFLECTION XAFS at AIR/WATER SURFACE

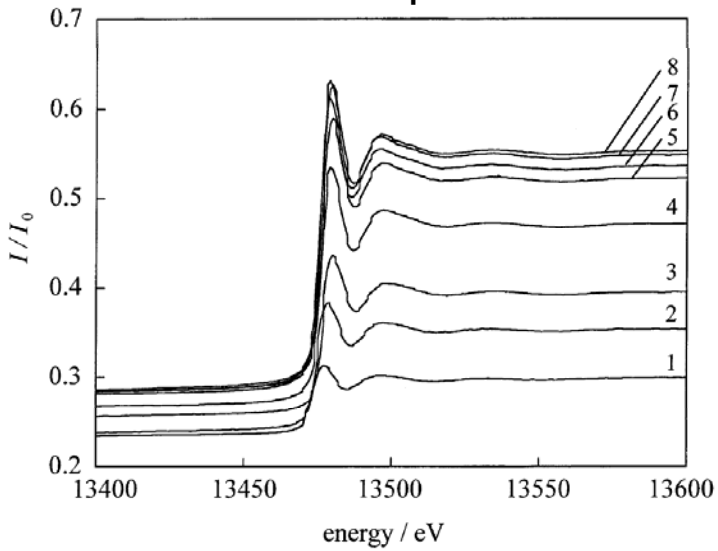
Surface tension vs. molality



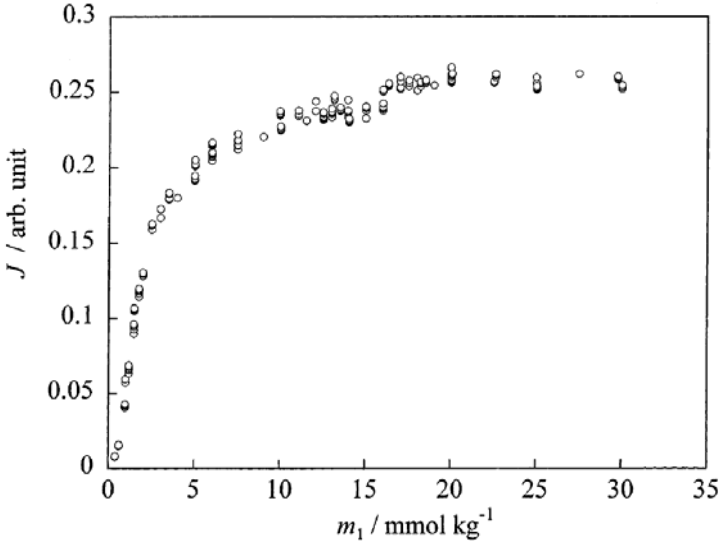
Surface density vs. molality



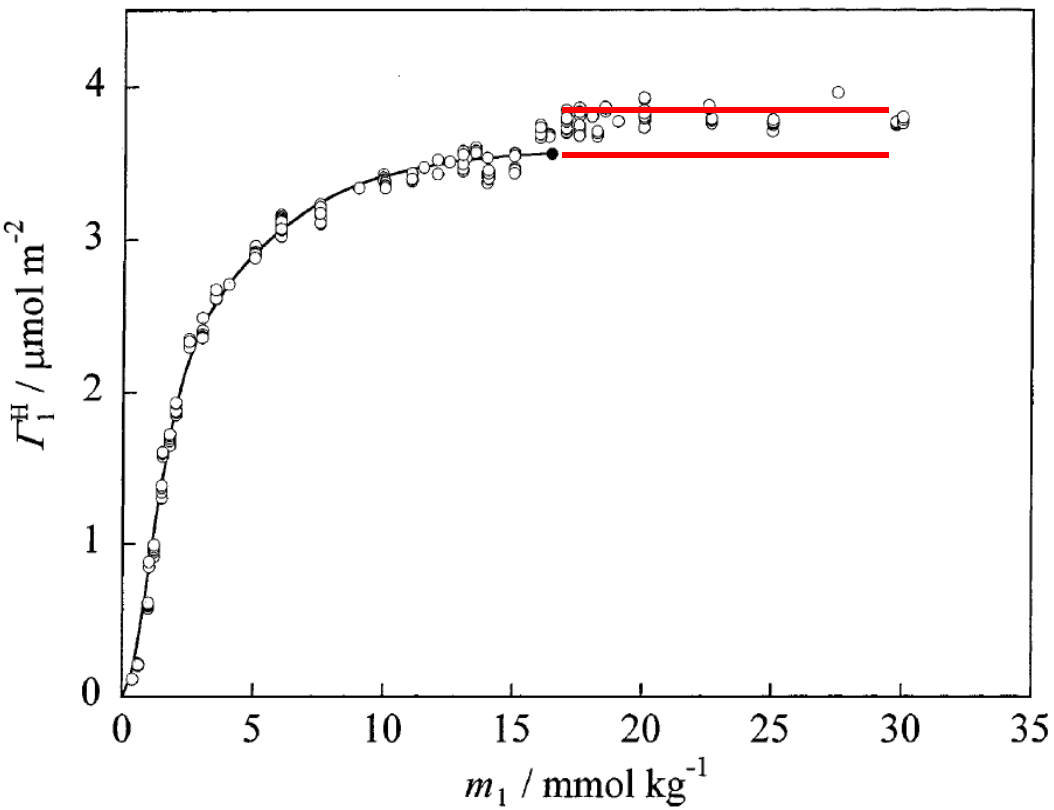
XAFS spectra



Jump vs. molality

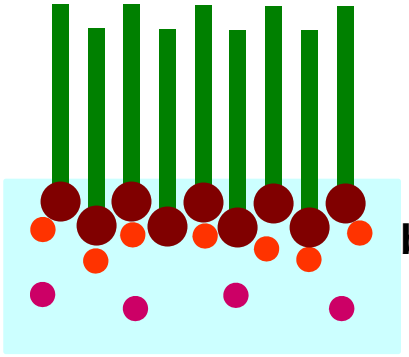


TOTAL-REFLECTION XAFS at AIR/WATER SURFACE



discrepancy between the Jump value and the surface density at around cmc

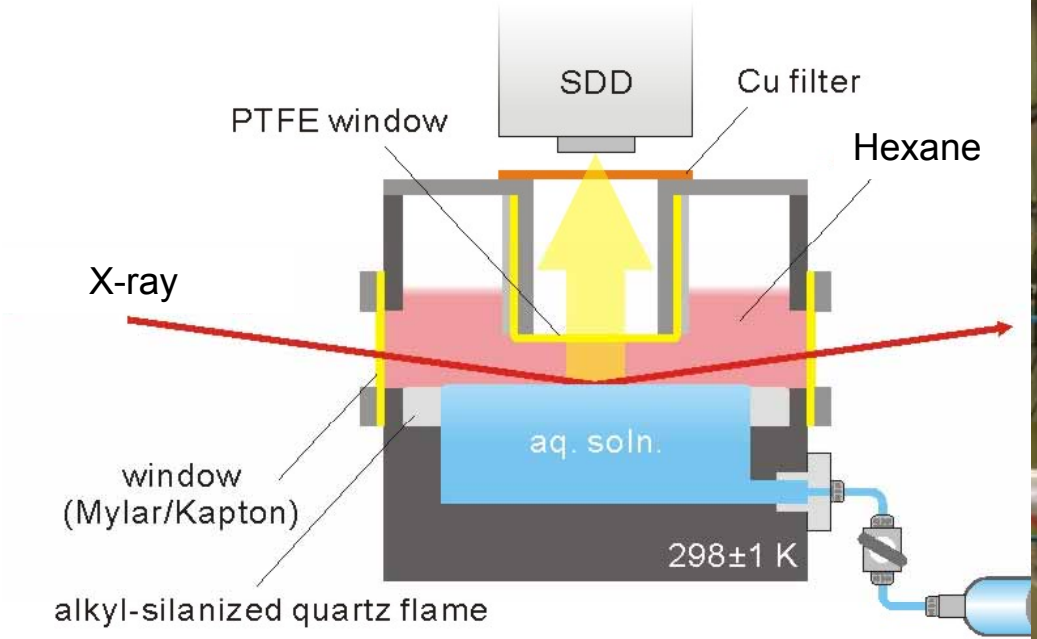
staggered arrangement of surfactant ions at the surface

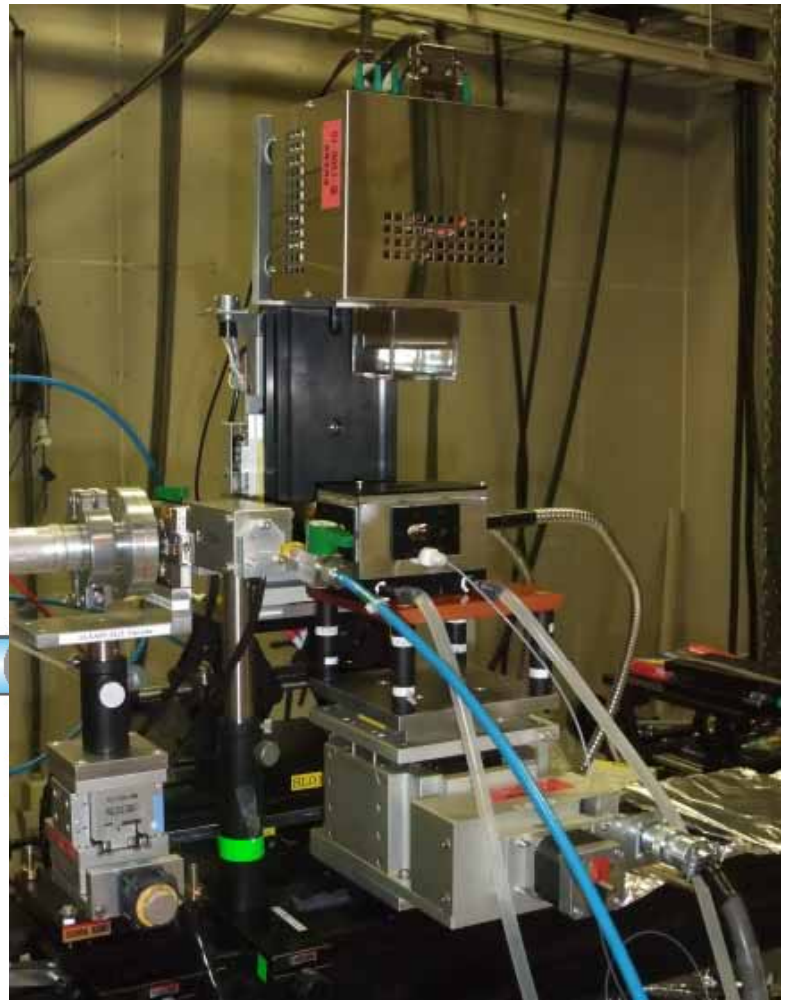


To know effect of oil on the arrangement of molecules at interface

TOTAL-REFLECTION XAFS at OIL/WATER INTERFACE

TR-XAFS set-up at BL39XU in SPring-8

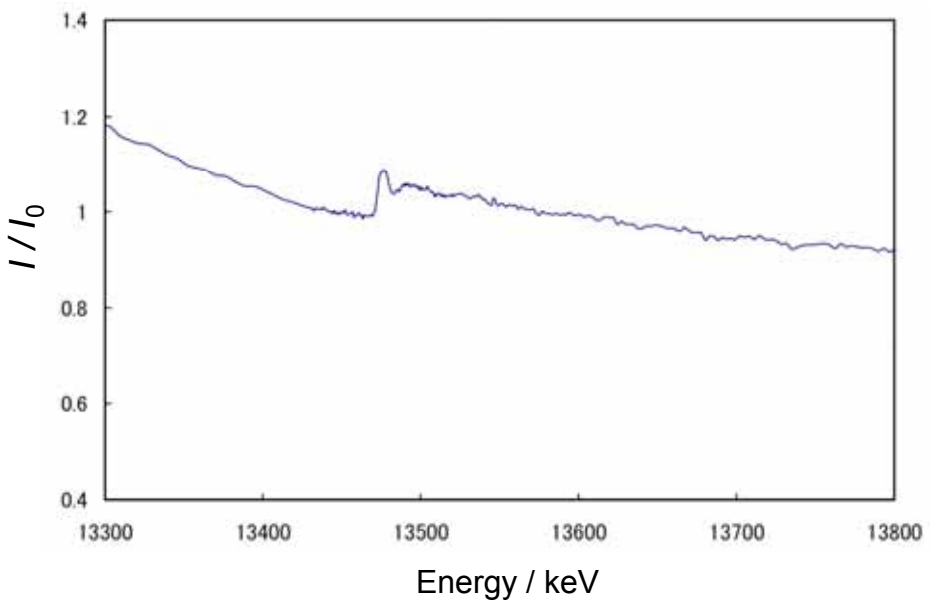




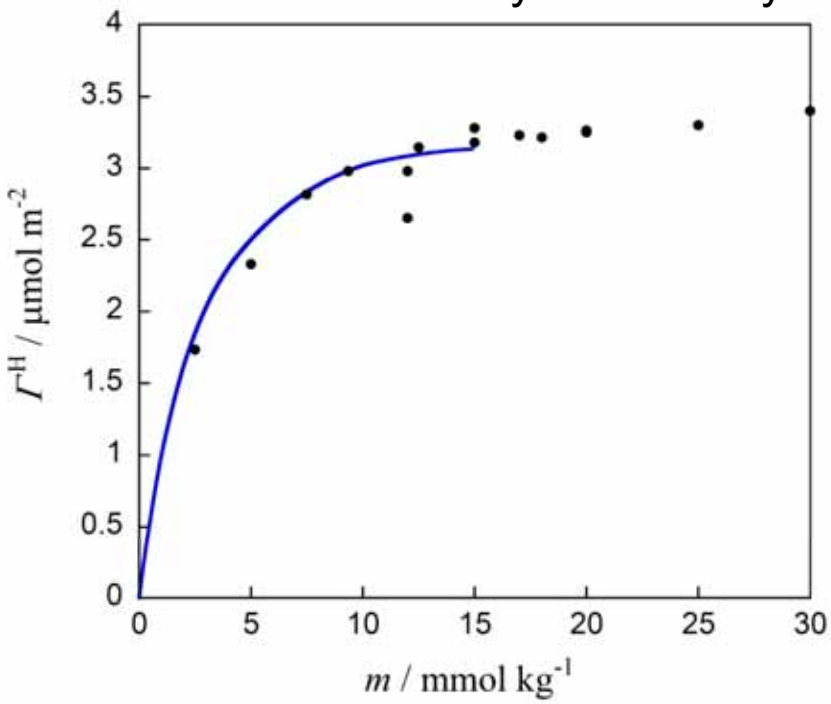
aq. DTAB solution / hexane

TOTAL-REFLECTION XAFS at OIL/WATER INTERFACE

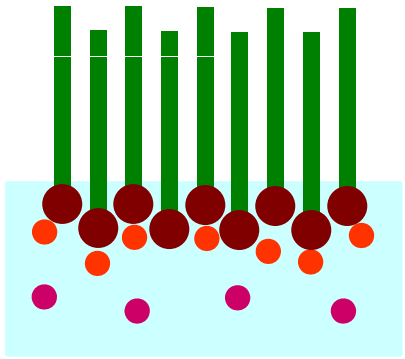
XAFS spectrum



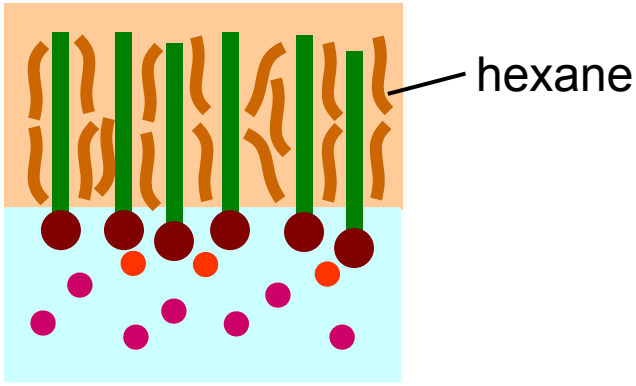
Interfacial density vs. molality



Air/Water surface



Hexane/Water interface



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