Olivier Diat, Jean-François Dufrêche, Agnès Grandjean,
Daniel Meyer, Serguei Nikitenko,Stéphane Pellet-Rostaing
Thomas Zemb

Cours de chimie séparative

2009-2010

La force d'hydratation : mythe ou réalité ?

Les deux (?) forces non-DLVO

Mesure dans des systèmes neutres

Se combine aux effets d'ions dans des systèmes chargés ?

Additivité des forces d'hydratation et de charge

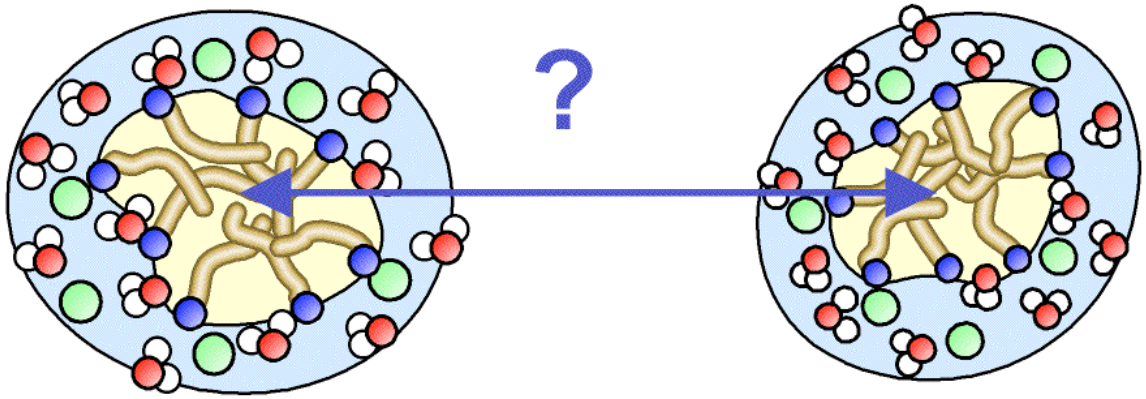
Quelles interactions

supra-moléculaires

colloïdales

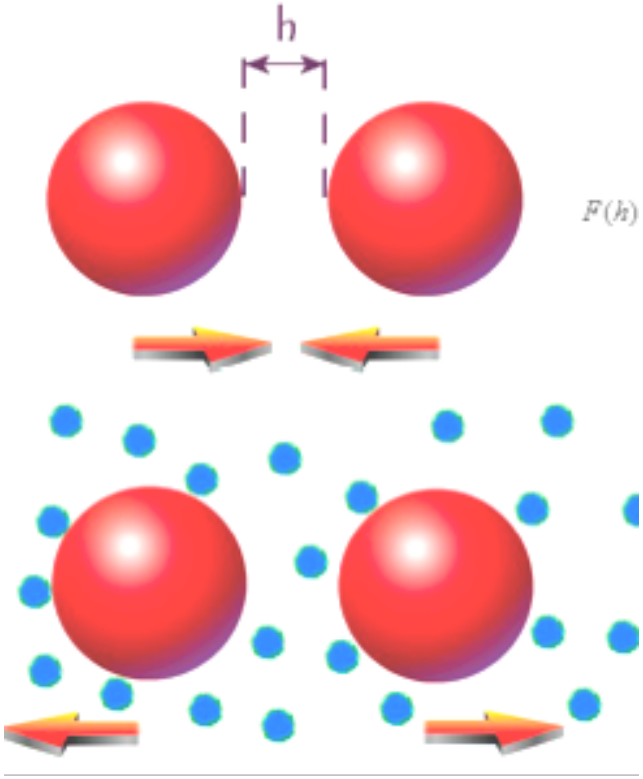
nanométriques

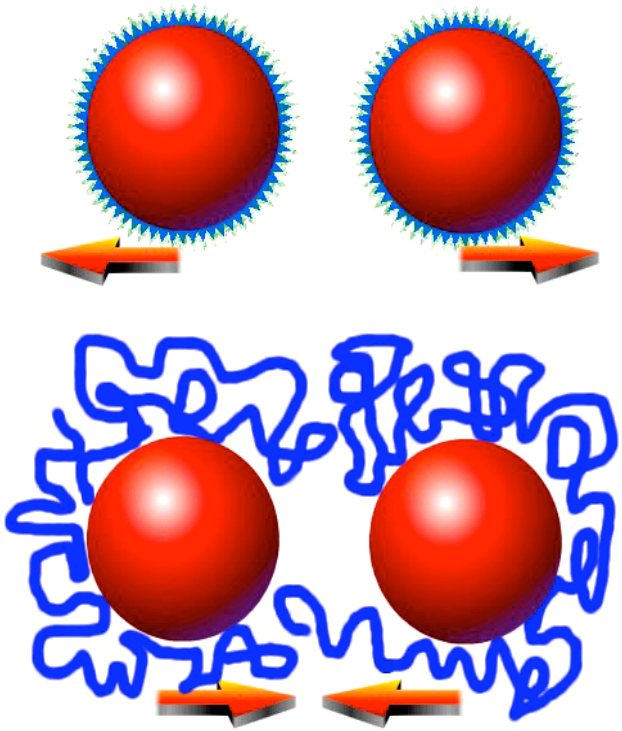
au-delà du premier voisin ? LRI



Forces faibles non-DLVO

Modélisation
Poisson-Boltzmann





« *Long range interactions in nanoscale science* »
R H French et V A Parsegian (2010) DOE-Dupont report

Pression répulsive entre bicouches neutres CiEj

$$\Pi = (RT/\overline{V}).\ln(p/p_0)$$

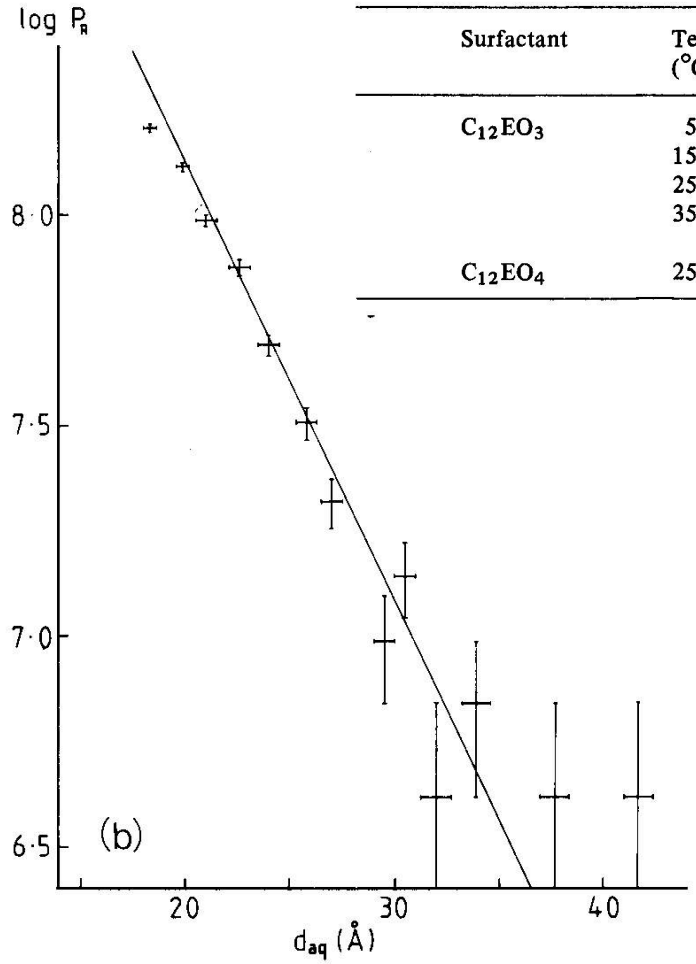
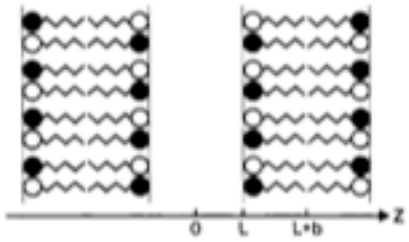


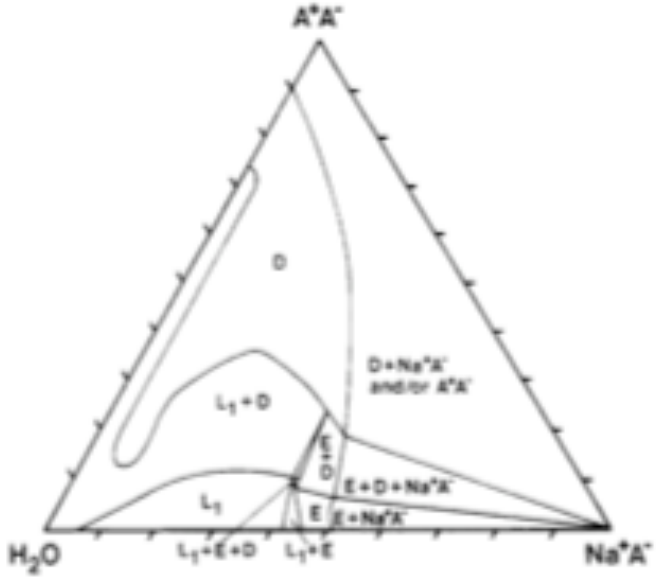
Table 1
Parameters used to fit vapour pressure data (P_0, λ for eq. (1); r, K_B, b for eq. (6))

Surfactant	Temperature (°C)	$10^{-10} P_0$ (dyne cm^{-2})	λ (Å)
$C_{12}EO_3$	5	11.5	2.9
	15	7.83	3.0
	25	7.10	3.1
	35	1.38	3.7
$C_{12}EO_4$	25	1.64	4.2

I.G. Lyle et G.J.T. Tiddy, Chem. Phys. Lett. (1986) 124n°5,432-437

Recherche de SMO sans effet stérique



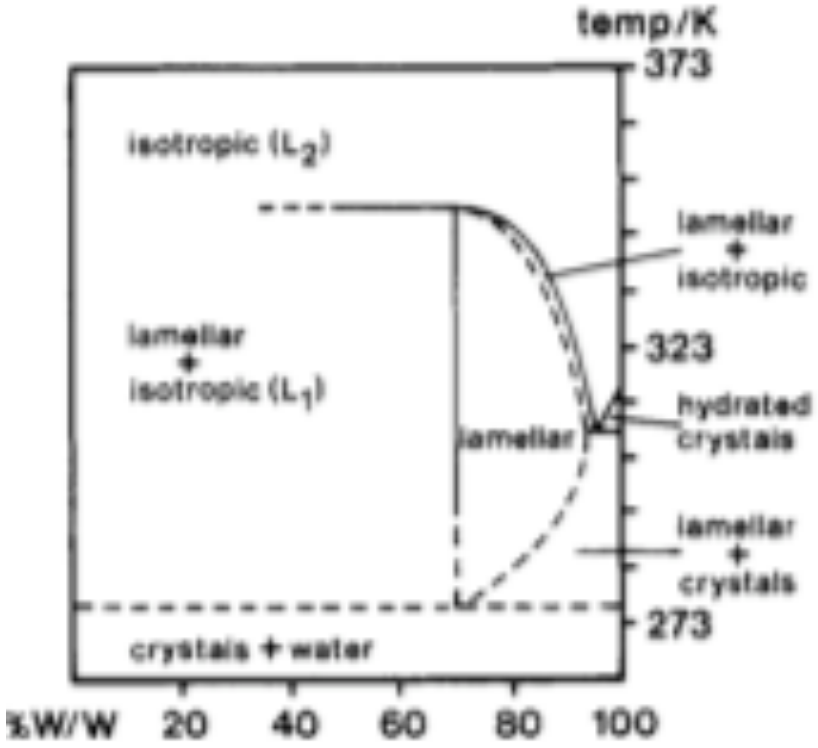


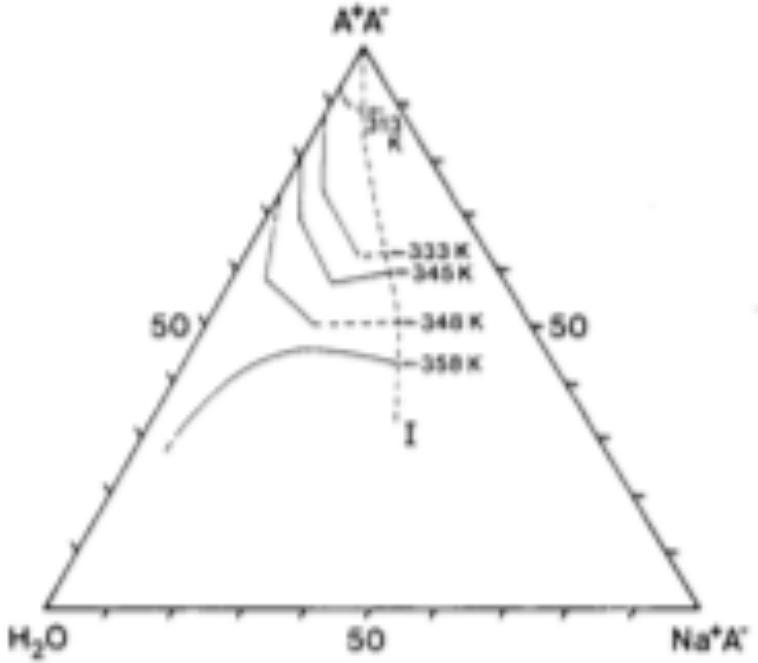
Octylammoniumoctanoate + Na-octanoate + eau

Diagramme de phases + dosages + pression binodales(EOS)

P. Jokela et al. , Langmuir 1988, 4, 187-192

Stabilité inattendue : vdW contre hydratation !





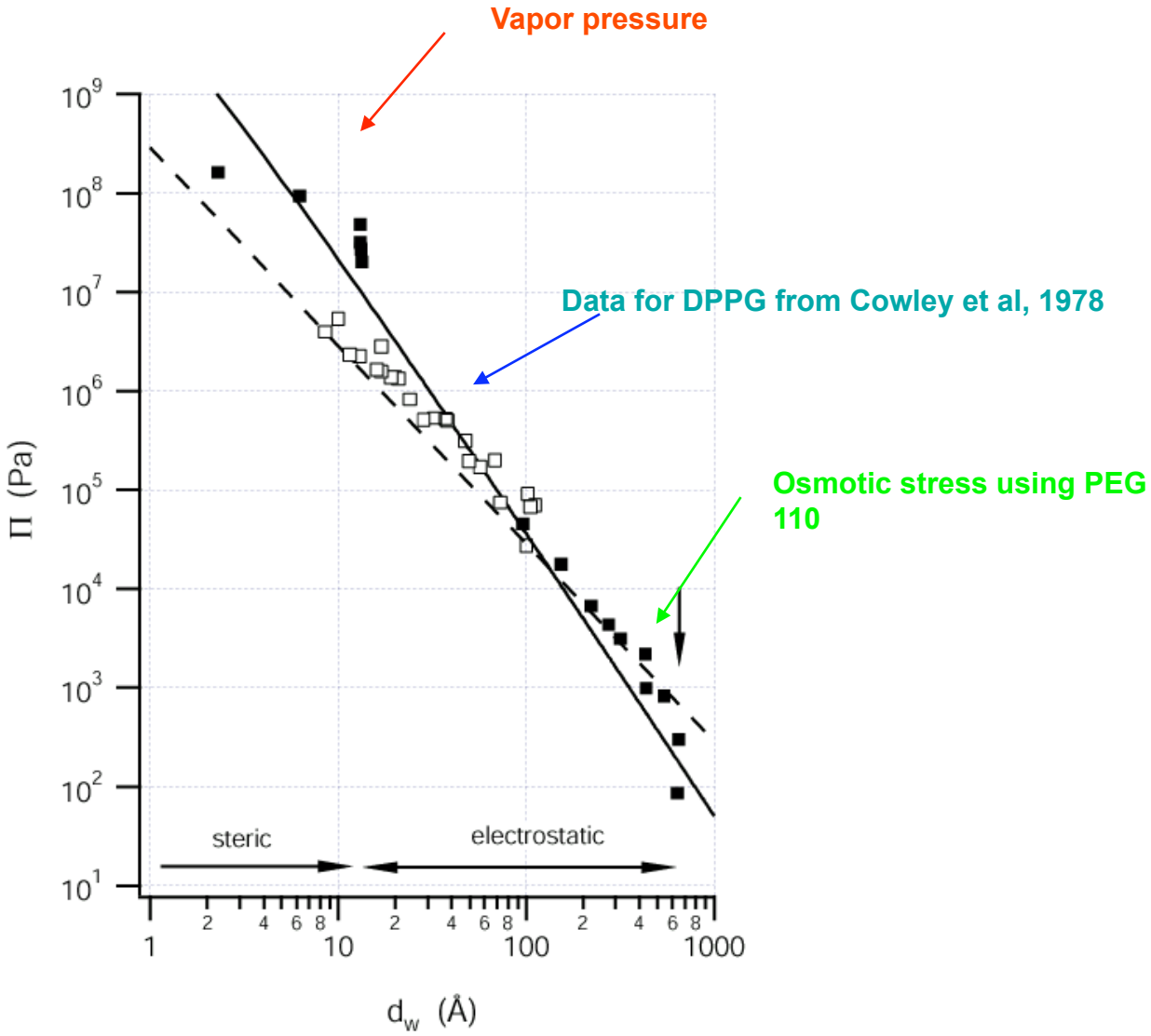
$$G/A = 5.5kT/\sigma .\exp(-h_A/1.25)$$

Cinq réferences de P. Jokela (>5000 refs litt.)

Revues: V A Parsegian

Prend le pas sur la force électrique: divergence ?

$$\Pi_e(d_w) = \frac{\pi k T}{2 L_B} \frac{1}{d_w^{\,2}}$$



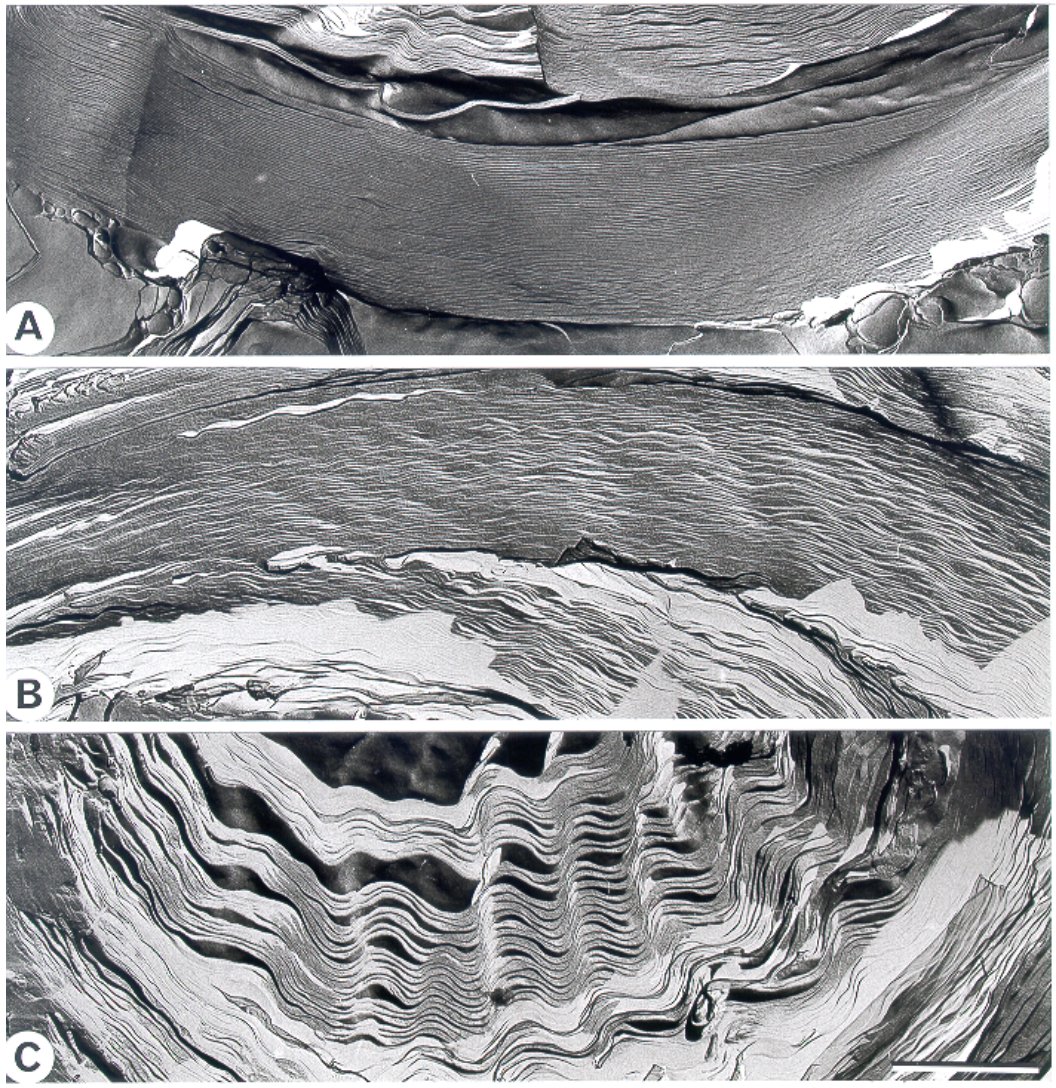
B. Demé et al. Langmuir, (2002) 18, 99-1004 et 1005-1013

Artefacts : Ondulation, protrusion ?

DOPS 30%

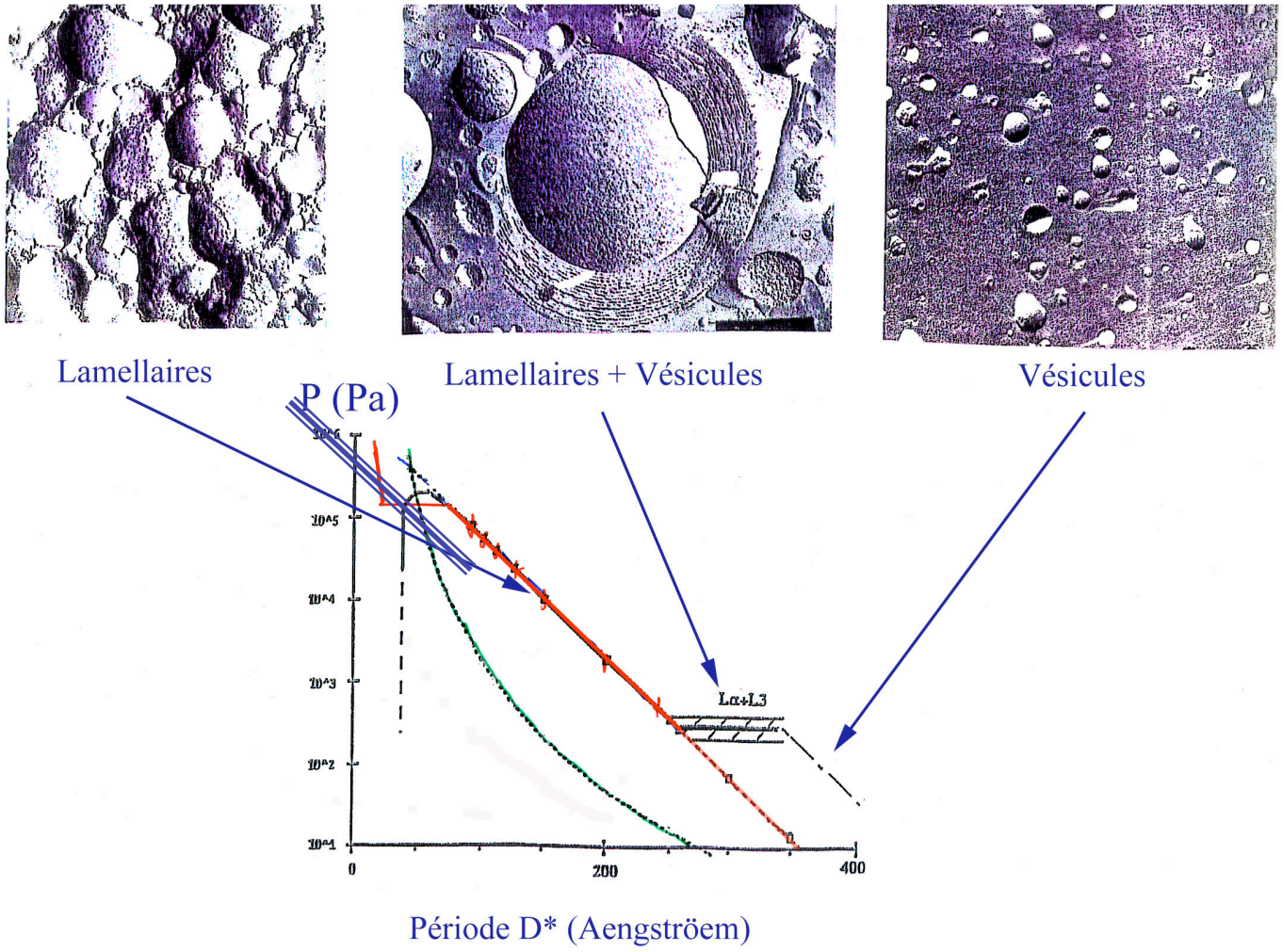
DOPS 14%

DOPS 5 %



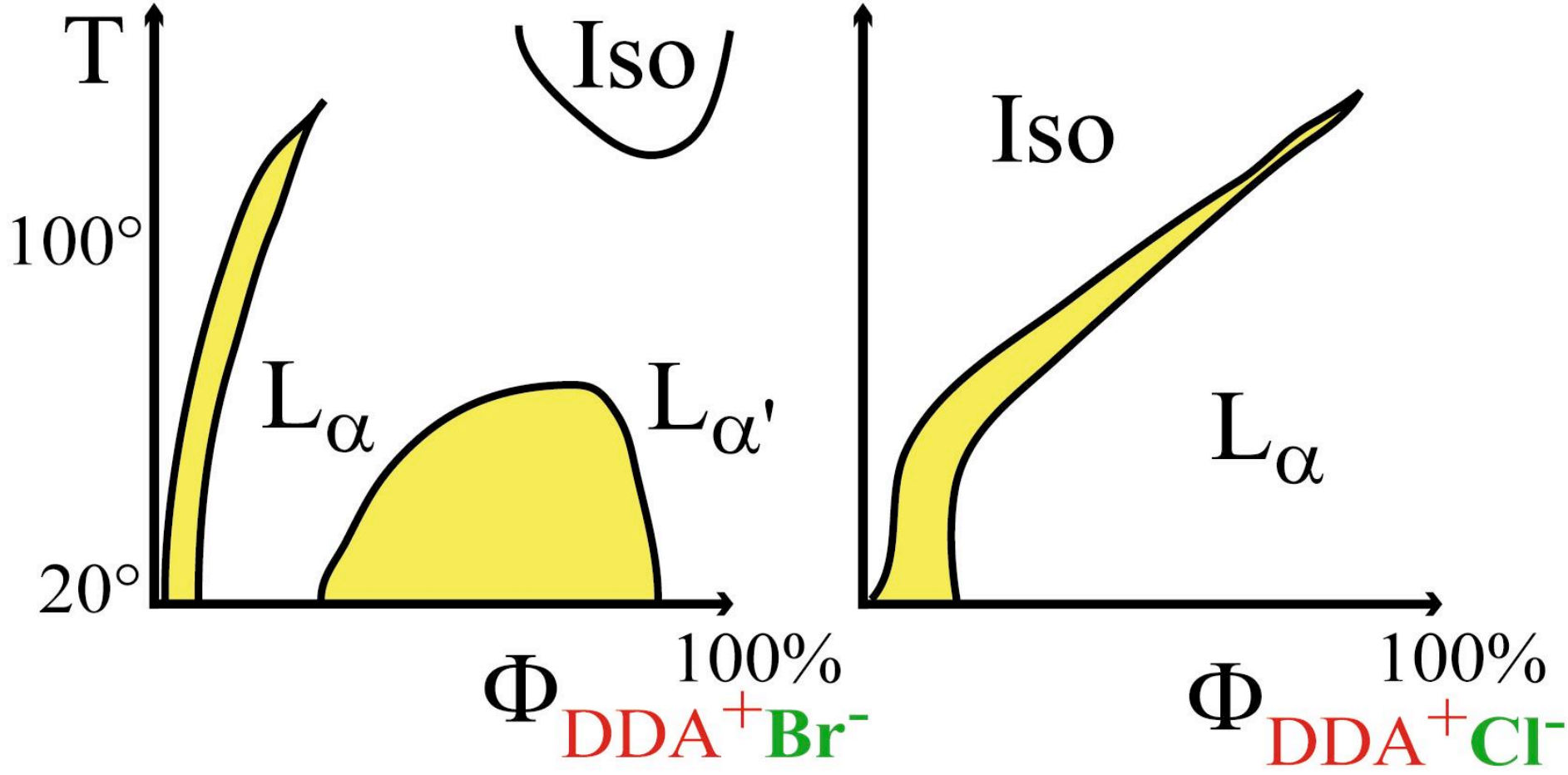
Revue: Current opinion in colloids and interfaces, 2000, 5, pp. 1-4.

Les deux limites : collapse et vésiculation



Revue: Current opinion in colloids and interfaces, 2000, 5, pp. 1-4.

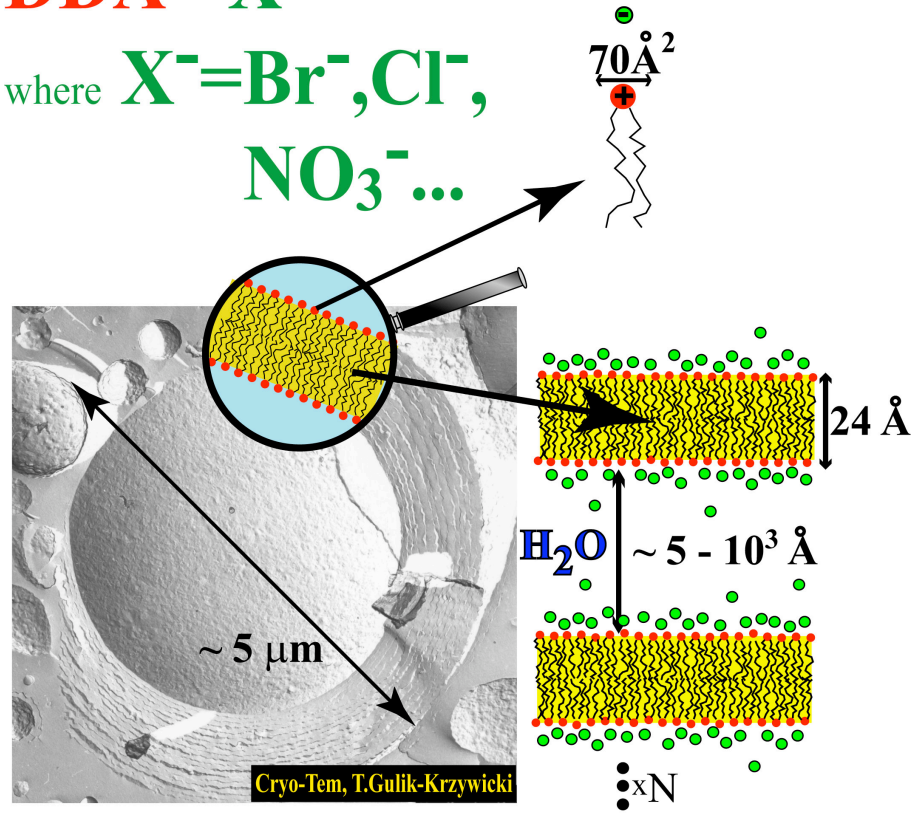
Phase Diagrams are counter-ion dependent



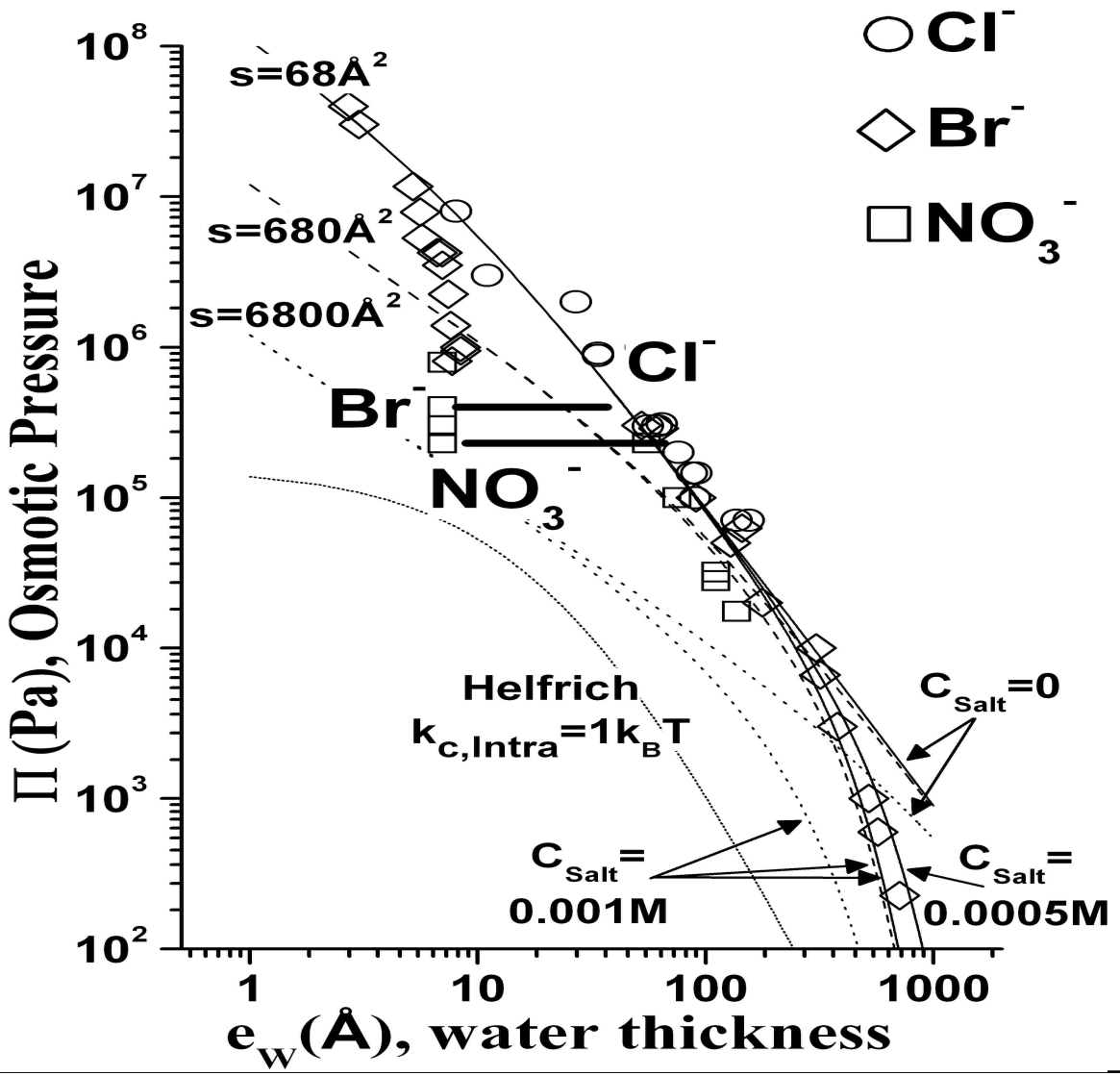
Equation d'état dépend de l'anion !!!!

$DDA^+ X^-$

where $X^-=Br^-, Cl^-, NO_3^-$...

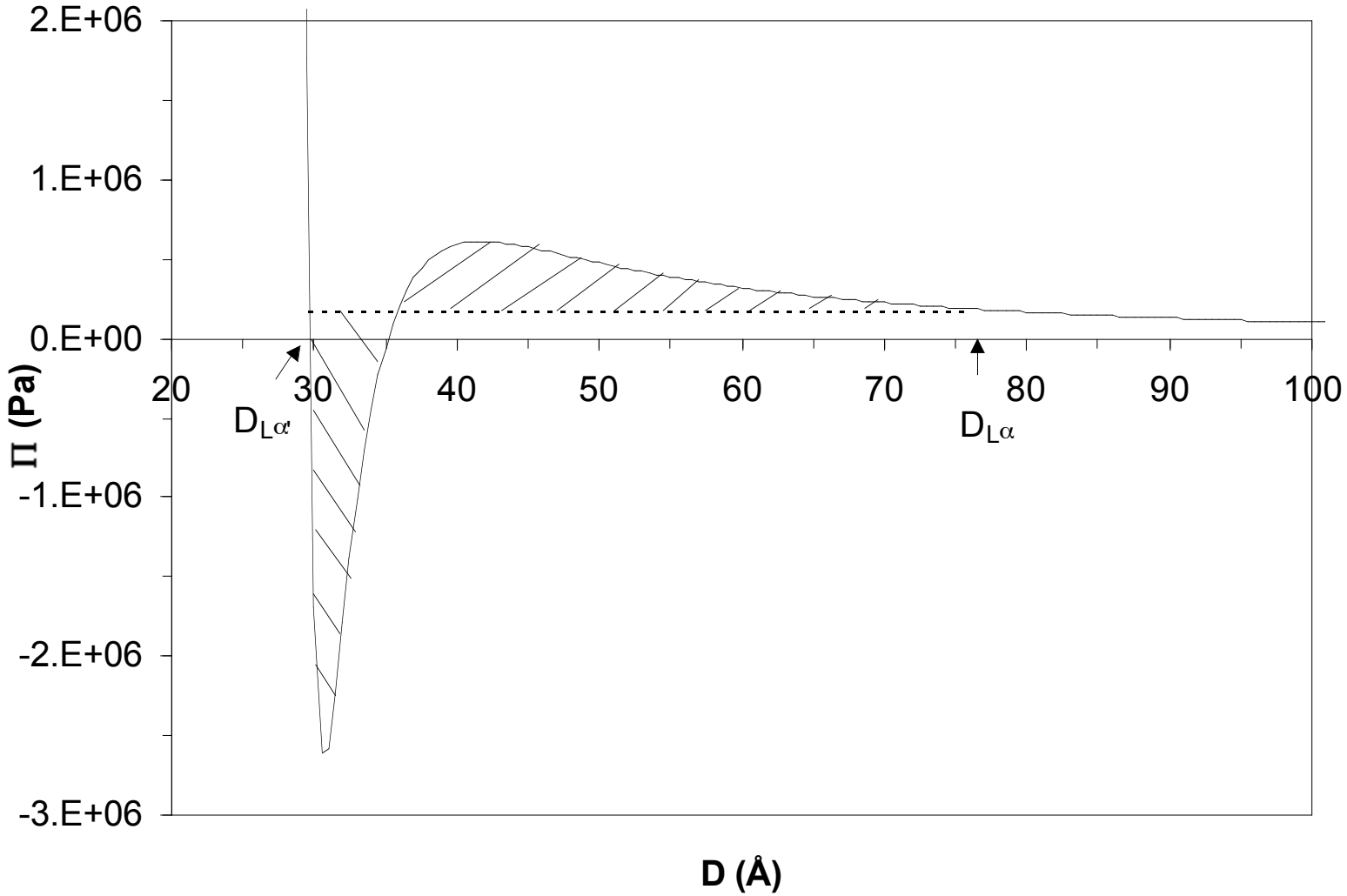


Effet des contre-ions chlore, brome, nitrate sur le gonflement



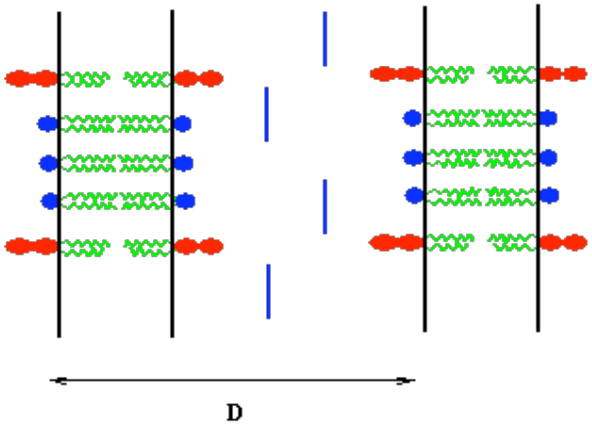
G. Brotons et al., Langmuir 2003 et J. Chem. phys. 2005

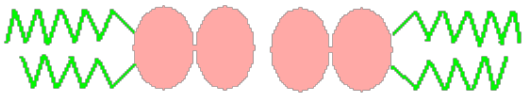
Explication: deux phases lamellaires en équilibre osmotique

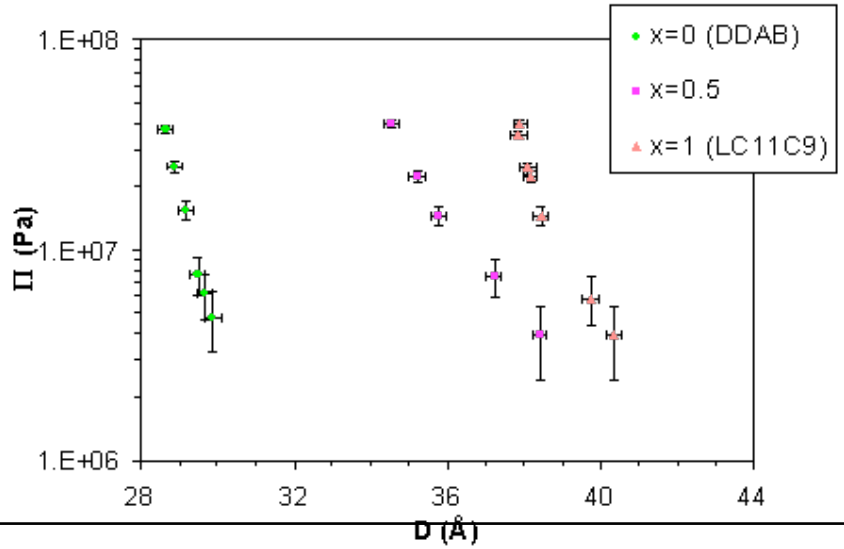


Th. Zemb et al., Progr. Colloid Polym. Sci. (1992) 89, 33-38

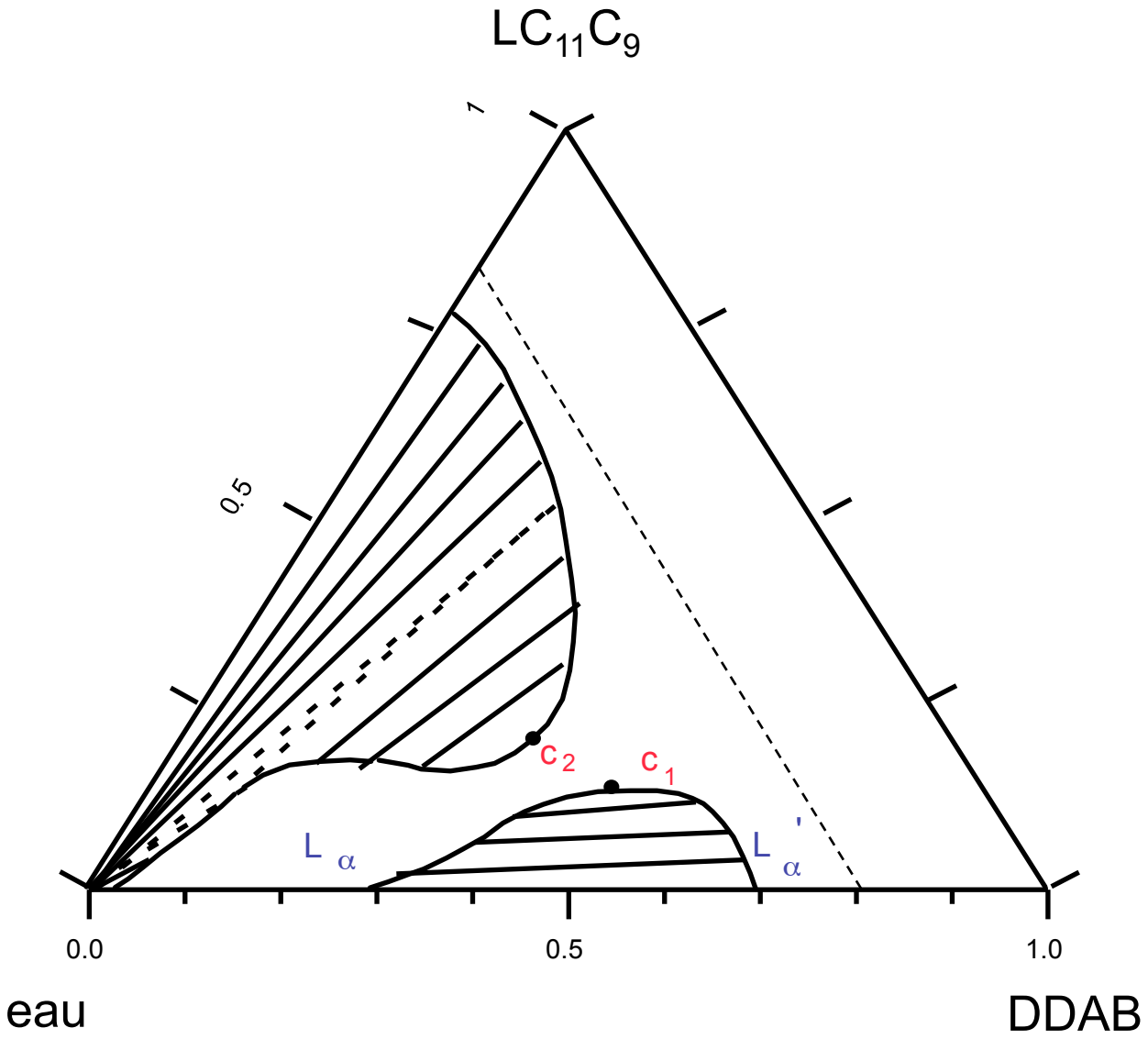
Et s'il y a avait deux tensioactifs ?



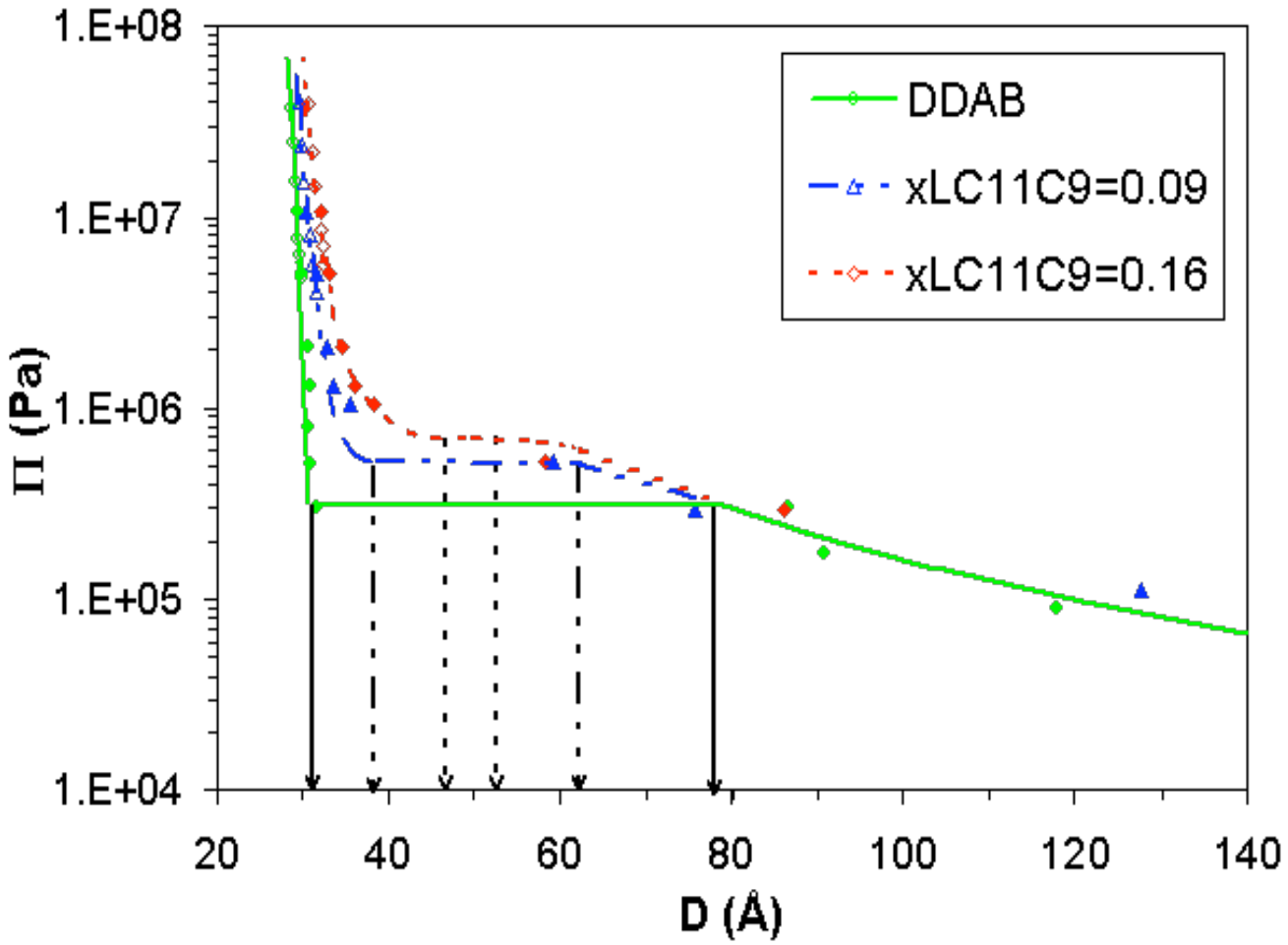




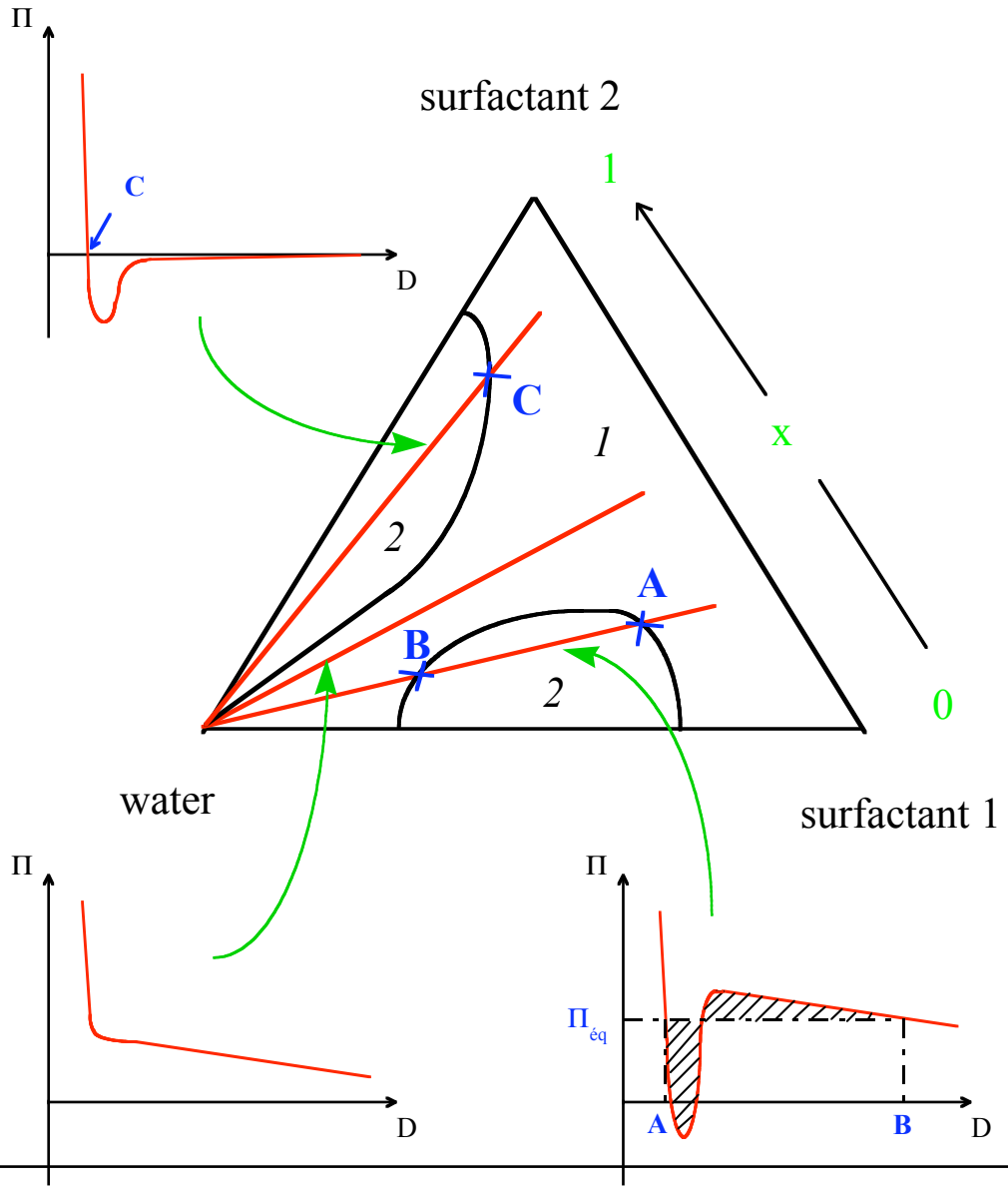
DEUX points critiques



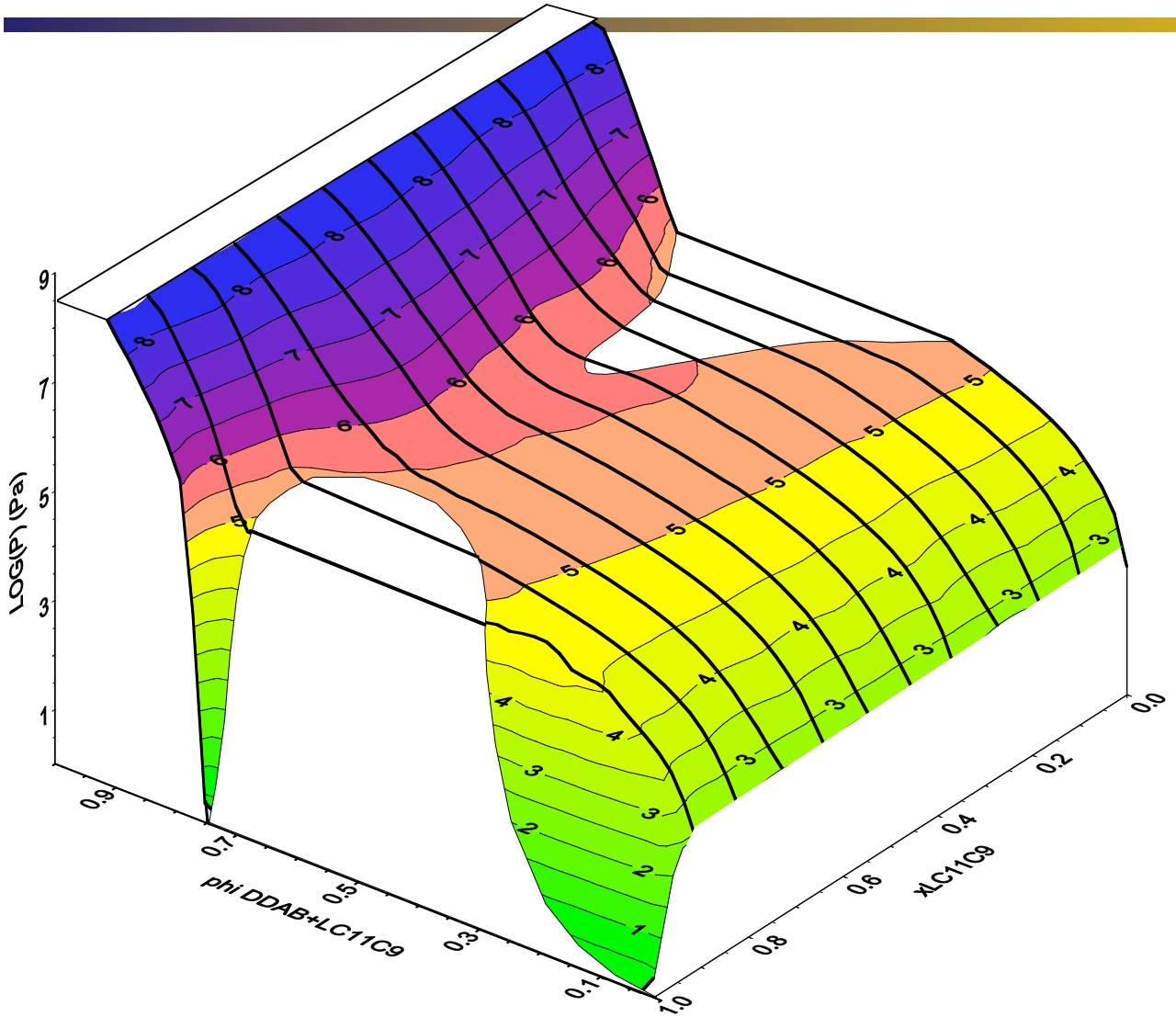
F. Ricoul, M. Dubois, Th. Zemb, M-P Heck, A. Vandais, D. Plusquellec, I. Rico-Lattes and O. Diat, J. Phys. Chem.B, 102, 1998, 2769-2775

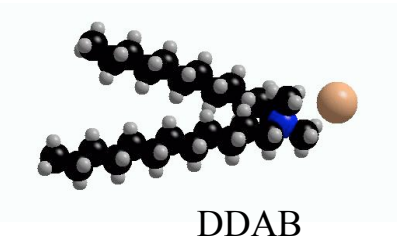

1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
Π (Pa)
20
40
60
80
100
120
140
D (Å)
DDAB
xLC11C9=0.09
xLC11C9=0.16

Deux répulsions, une attraction....

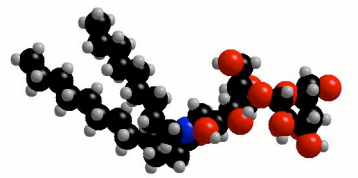


F. Ricoul, M. Dubois, L. Belloni, Th. Zemb and I. Rico-Lattes,
Langmuir, 14, 1998, 2645-2655





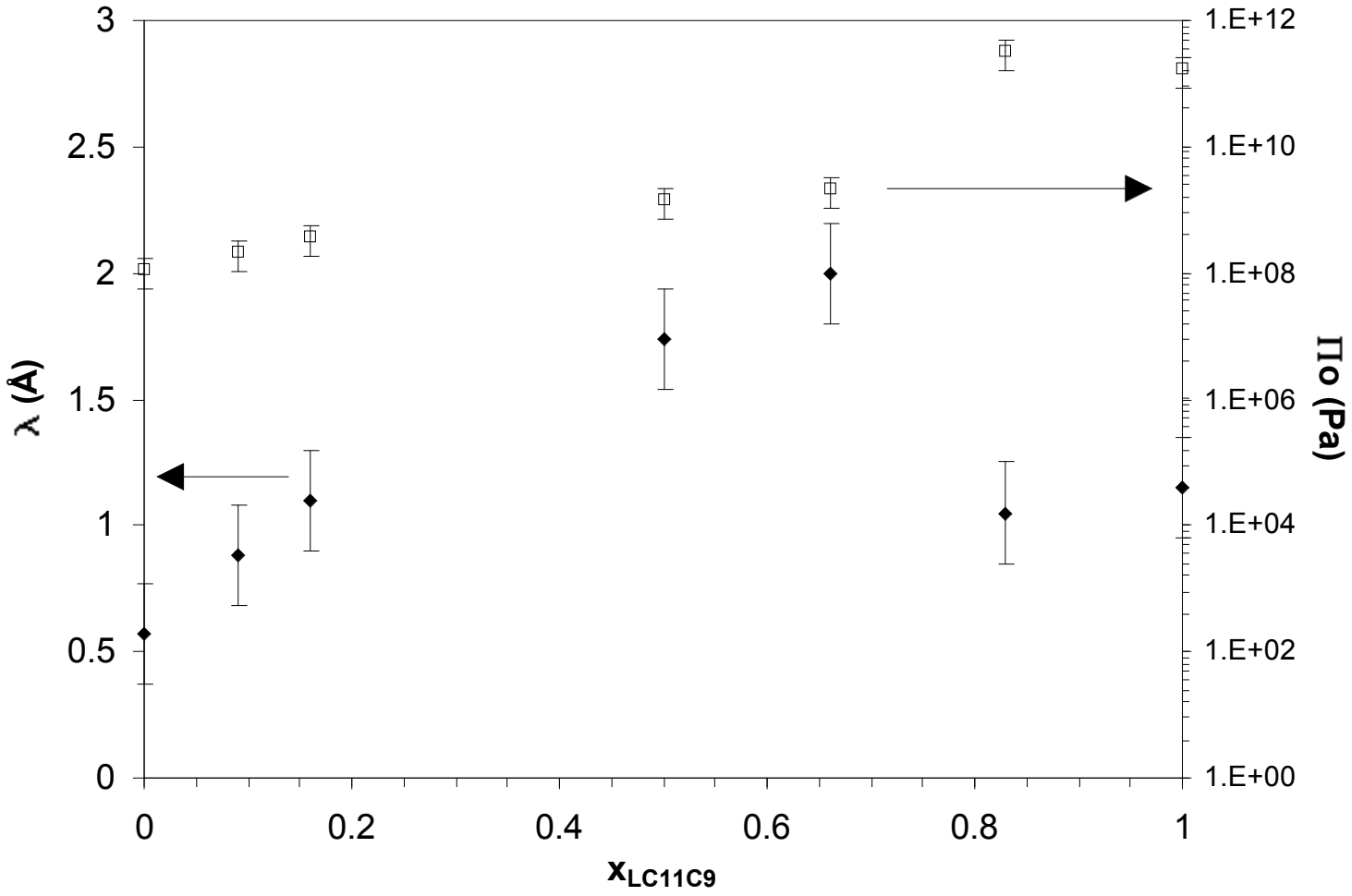
DDAB



Uncharged glycolipid

F. Ricoul, M. Dubois, L. Belloni, Th. Zemb and I. Rico-Lattes,
Langmuir, 14, 1998, 2645-2655

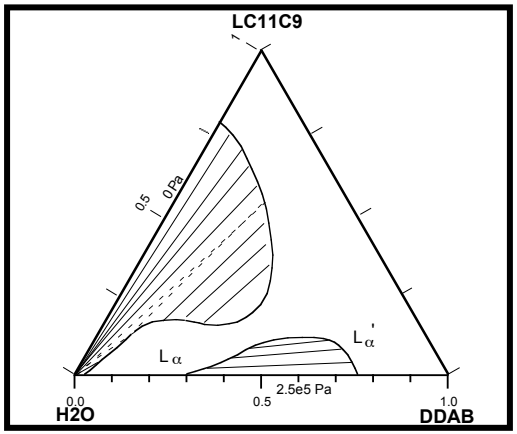
Premières mesures de portée et pression au contact

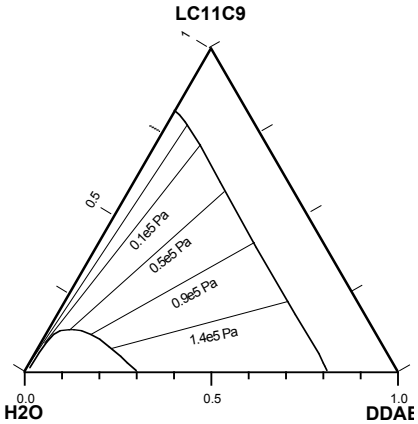


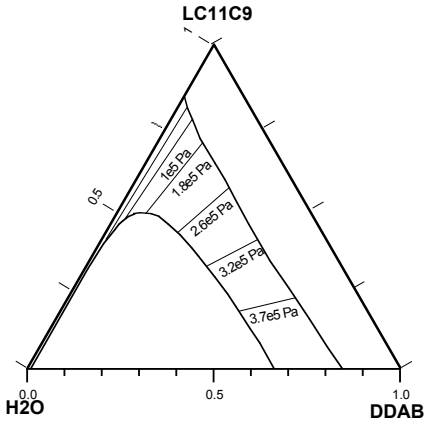
Confrontation aux théorie(s) proposées:

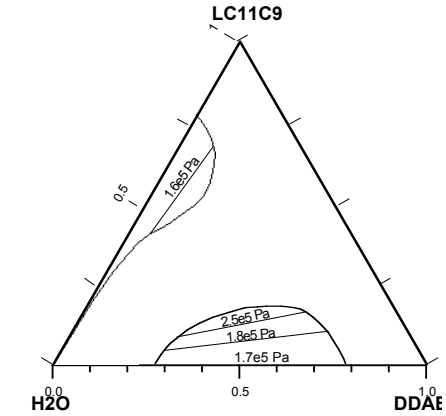
Hydration, ion affinity, vdW
unchanged upon grafting of sugar

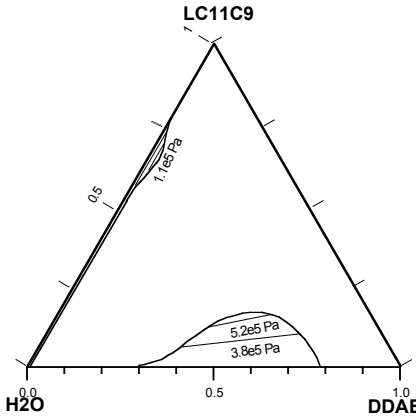
Same , unchanged from pure
C11-C9 case

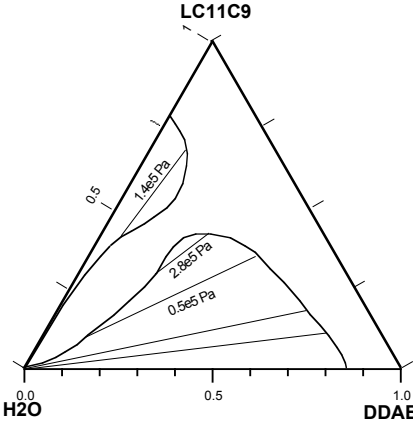












Vary hydration by
Extrapolation from low water content

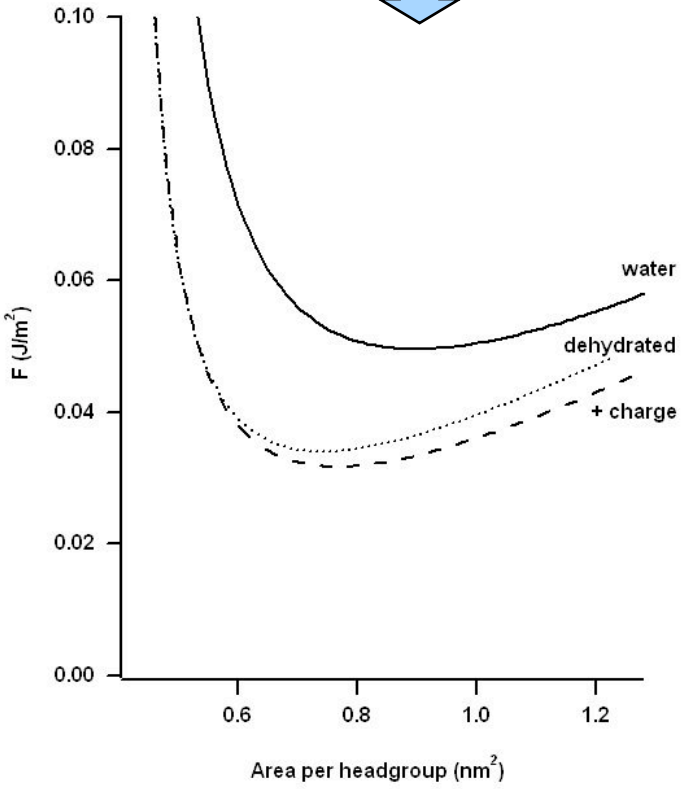
Idem with constant attractive terms
as pure glycolipid

+ adhesion energy 10^8Pa*3A*
Mole fraction dependant (stickers!)

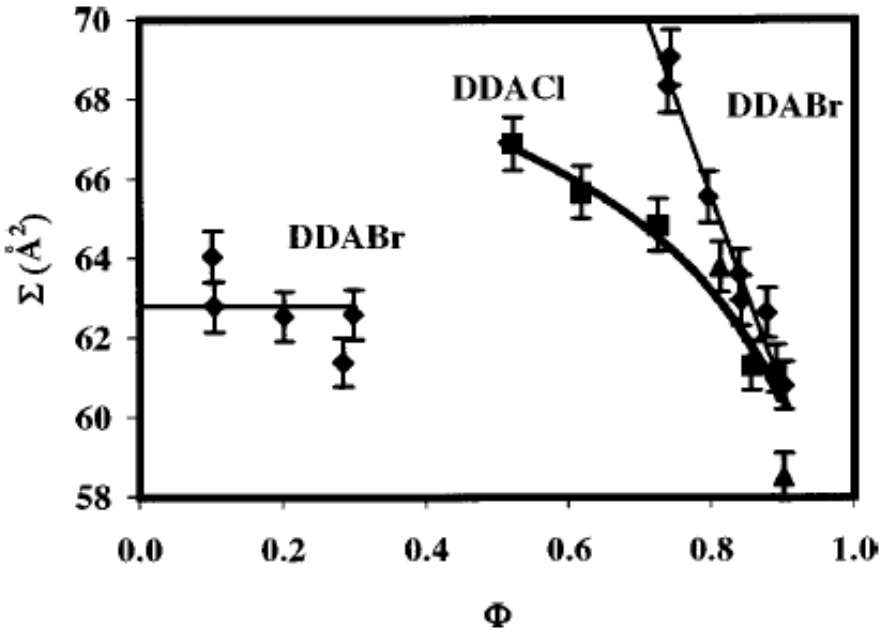
F. Ricoul, M. Dubois, L. Belloni, Th. Zemb and I. Rico-Lattes, Langmuir, 14, 1998, 2645-2655

Hydratation et équation d'état latérale ?

$$F_{mole} = \gamma(a - a_0) + \frac{C(\mu_{H2O})}{a - a_0} + F_s + F_{el}$$

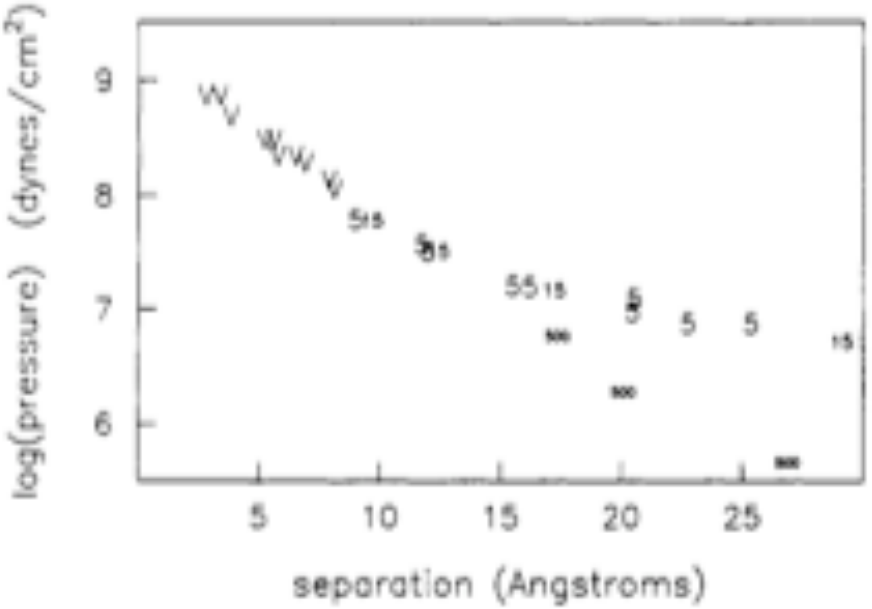


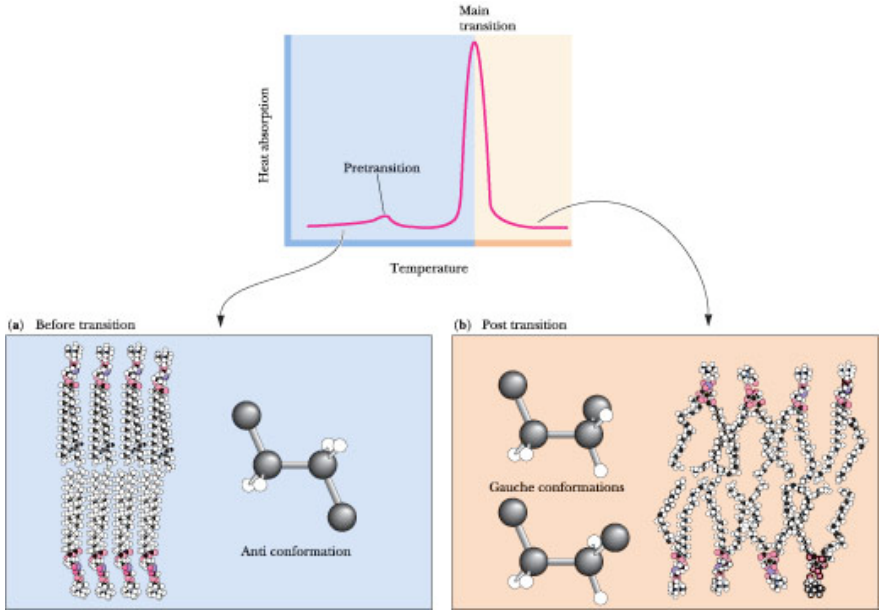
J. Chem. Phys., Vol. 108, No. 18, 8 May 1998



Transitions dans les systèmes vitreux ?

Un résultat inattendu avec un gel d'acetate !





Transitions dans les colloïdes « vitrifibiables ».

VA Parsegian et al., J. Phys. Chem. 1991, 95, pp.4777-4582