ELECTROSTATIC INTERACTIONS

Applications in colloid science

Overbeek Medal Lecture

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Motivation

Electrostatic intermolecular interactions
are the most important cause of molecular
organization and selectivity in
biological and colloidal systems

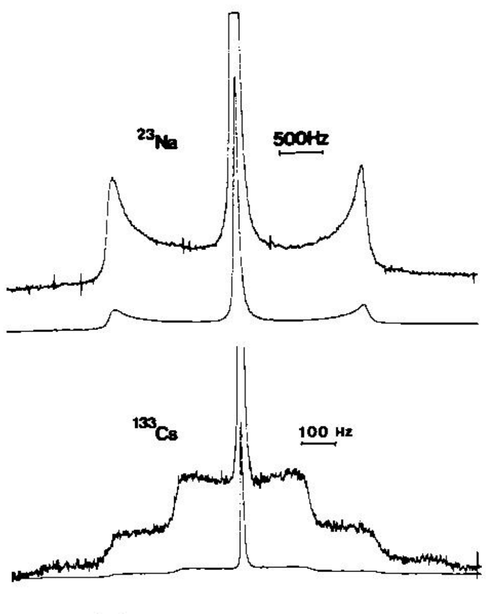
Strategy

Combine theory and experiment.
Study model systems that can illustrate theory.
Combine molecular, colloidal and thermodynamic
perspective.
Demonstrate relevance for some applications.

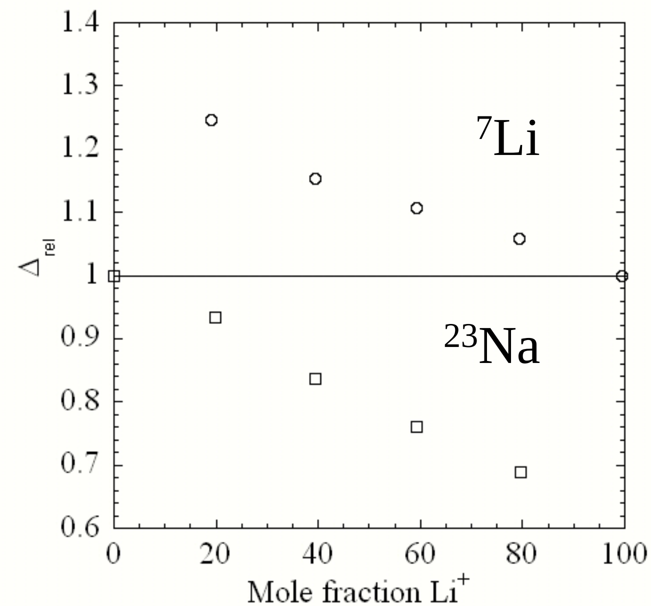
Counterion NMR

Question:How are counterions interacting with highly charged surfaces?

Approach:Measure quadrupolar splittings for lamellar liquid crystals



Na^{+} vs Li^{+} competition



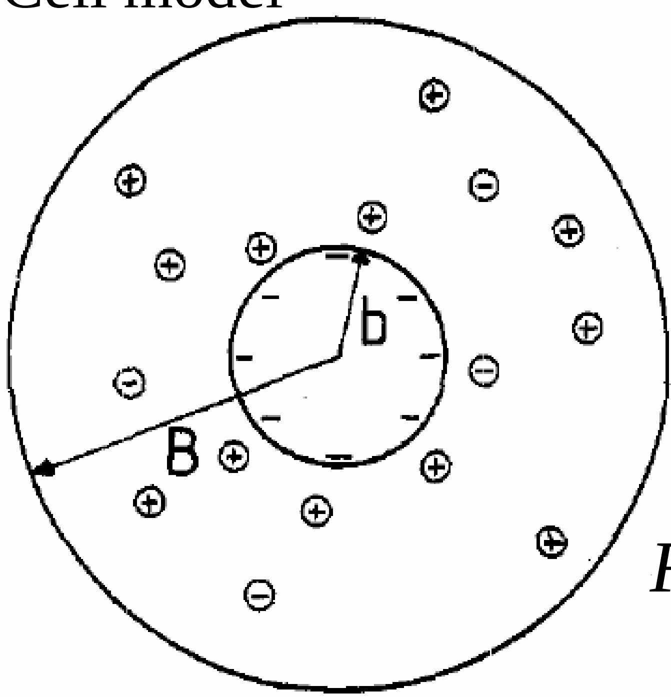
Söderman,Engström&HW J.Colloid.Interfacce Sci 1980

The Poisson-Boltzmann equation and the cell model

Mean field free energy functional

$$A_{el} = \tfrac{1}{2}\int \rho\Phi dV - k\sum_i \int c_i(\ln c_i - 1)dV - n_i\{\ln(n_i/V) - 1\}dV$$

Cell model



Minimization leads to:

Poisson-Boltzmann equation

$$\varepsilon_0\varepsilon_r\nabla^2\Phi = -e\sum_i z_i c_{i0}\exp(-z_i e\Phi/kT)$$

Contac value theorem:

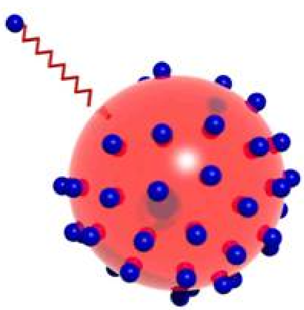
$$Force/area = kT\sum_i c_i(z_w) - \sigma_w/(2\varepsilon_0\varepsilon_r)$$

HW,Jönsson,Linse J.Chem. Phys.1982

Ionic amphiphiles 1

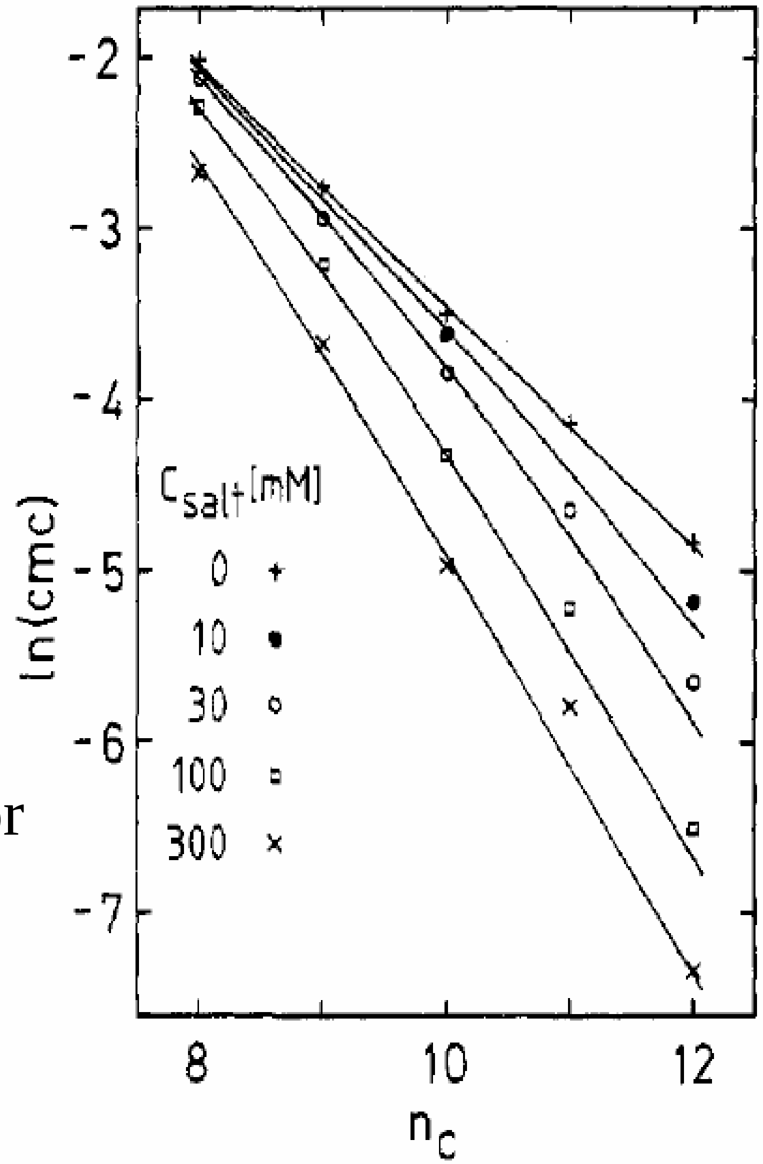
Question:What is the electrostatic contribution to the formation of a micelle?

Approach: Solve the PB equation.



Gunnarsson, Jönsson,HW
J.Phys.Chem 1980

Theory and experiment for CMC of alkyl sulfates

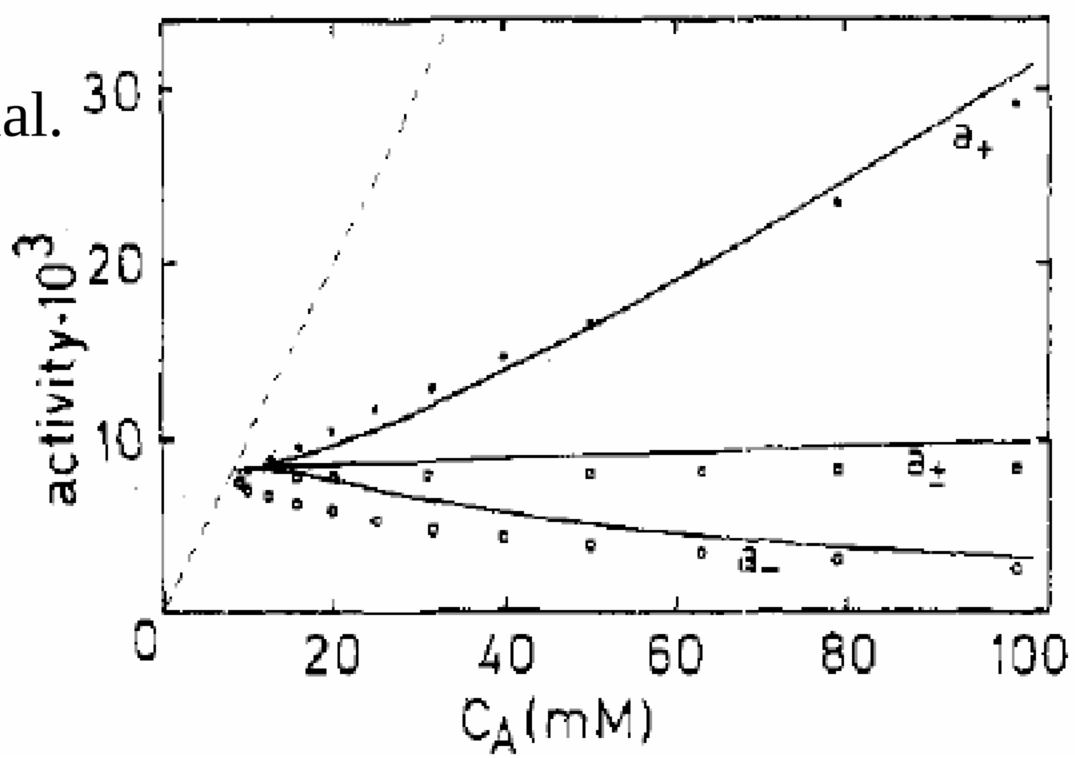


Ionic ampiphiles 2

Q:Micelle-micelle interactions?

Theory and experiment
For SDS

A:PB equation.Cell model.
Test for ion chemical potential.



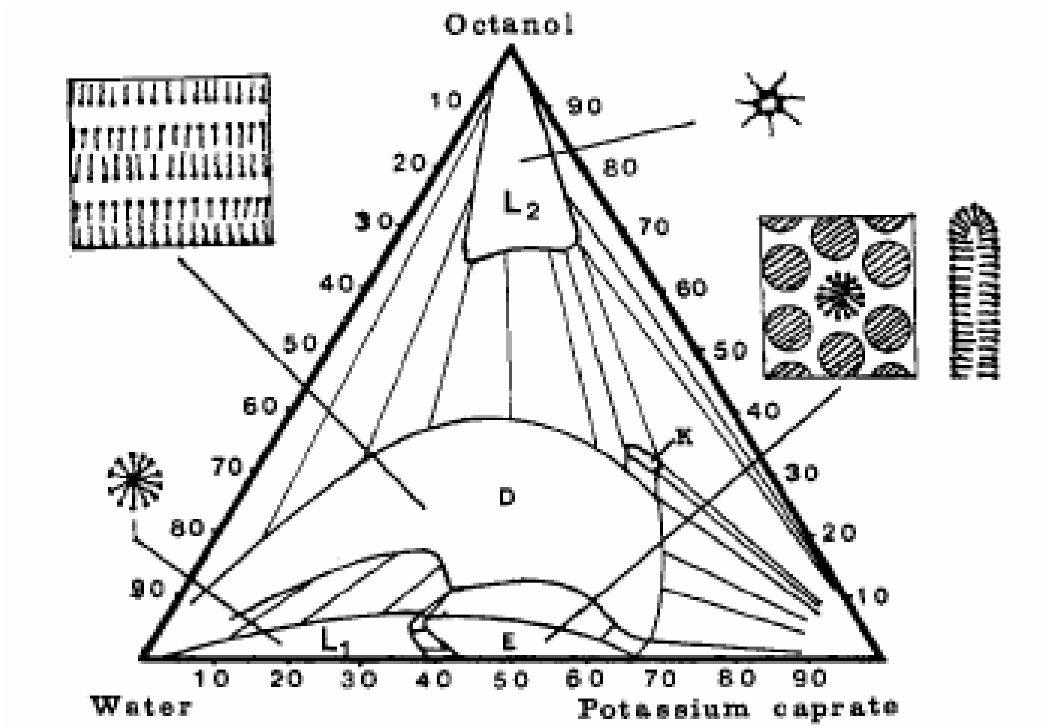
Gunnarsson, Jönsson,HW
J.Phys.Chem 1980

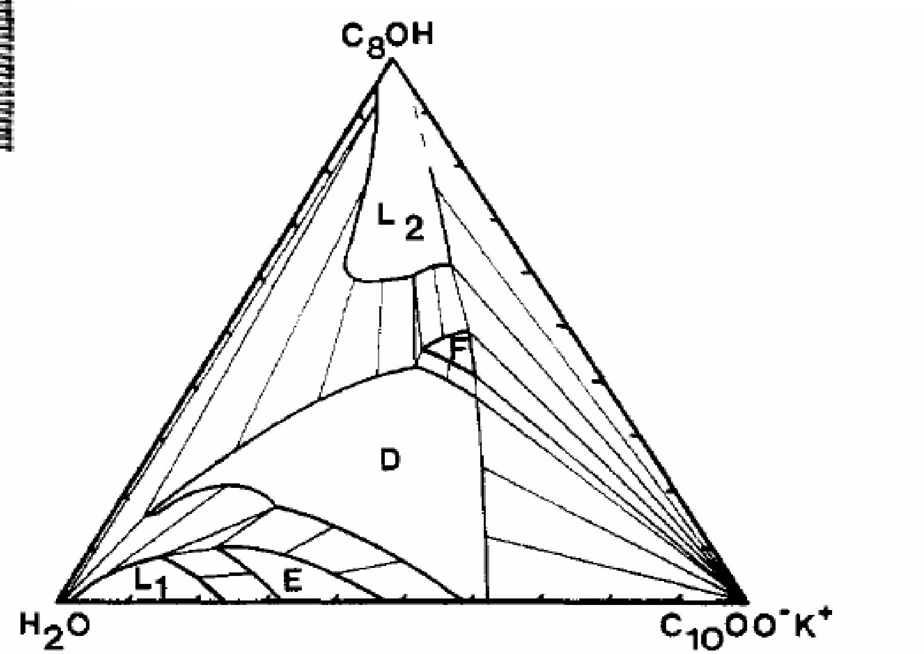
Ionic amphiphiles 3

Q:Is phase behavior driven by electrostatics?

A:Create model free energy.

Calculated phase diagram!



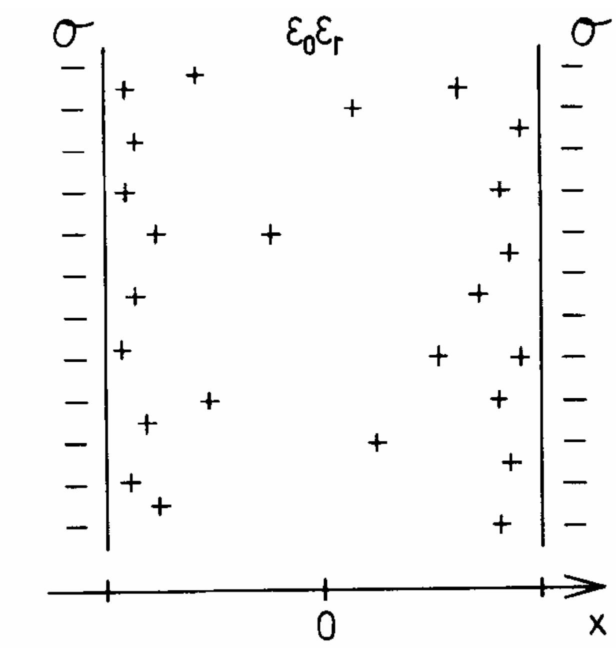


Jönsson,HW J.Phys Chem 1987

Ion Correlations 1

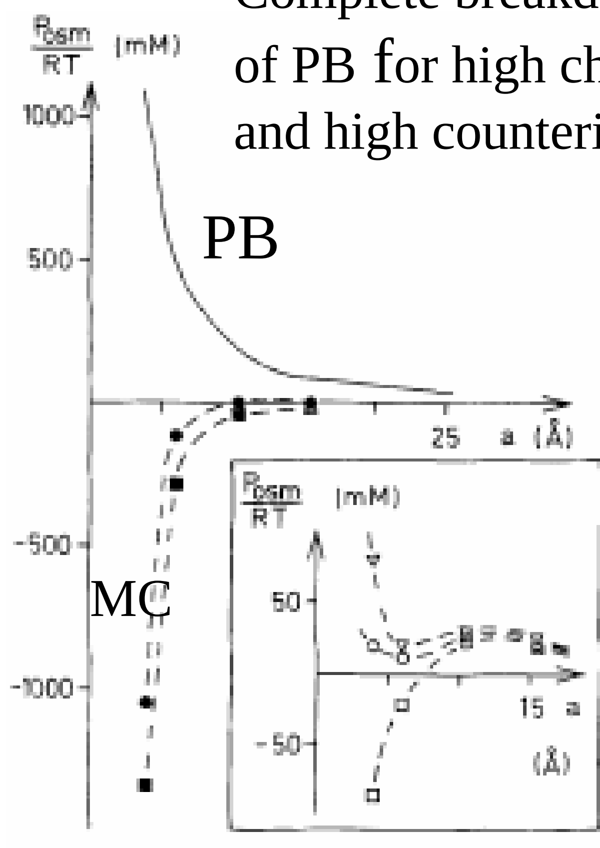
Q:Accuracy of mean field approximation?

A:MC simulations!



Model:Planar charged walls.
Only counterions

Complete breakdown
of PB for high charge densities
and high counterion valencies



Non-monotonic
force curve
in transition region

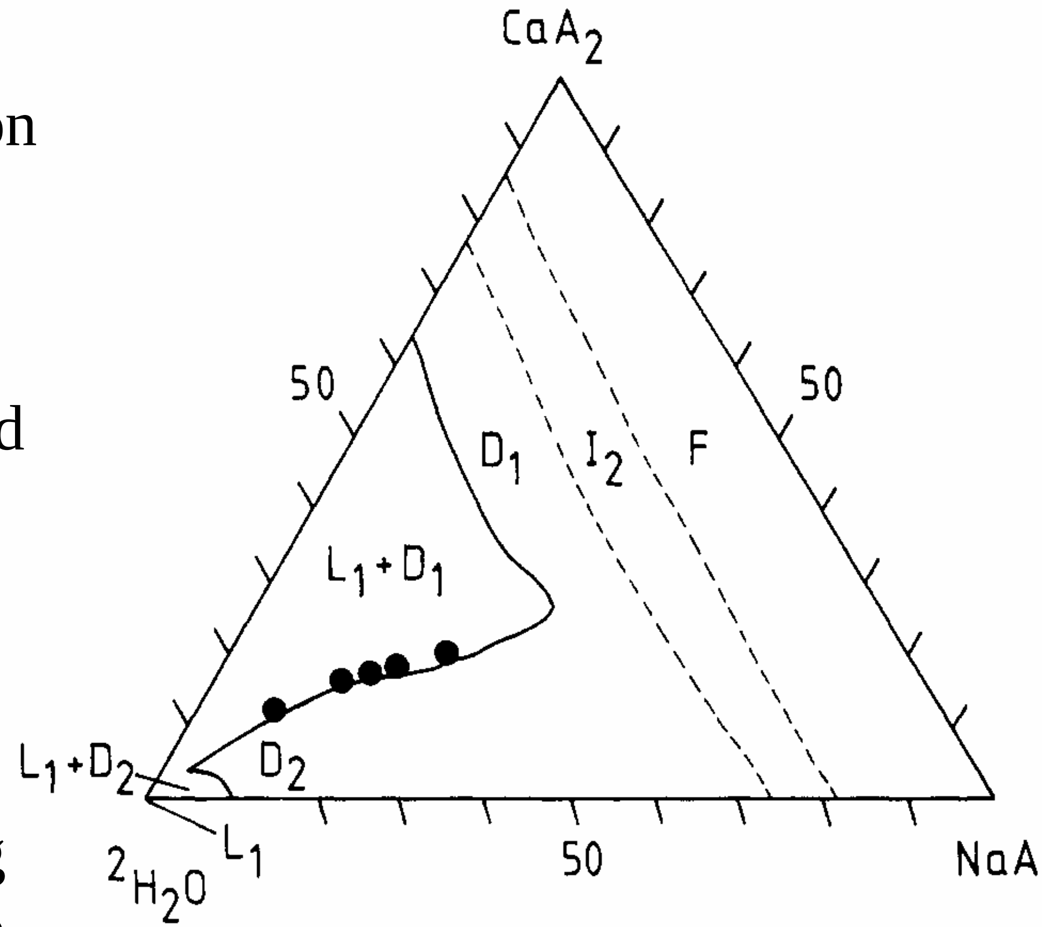
Guldbrand,Jönsson,HW,Linse J.Chem.Phys. 1984

Ion correlations 2

Q:Experimental manifestation of correlation attraction?

A:Compare lamellar liquid crystals with monovalent and divalent counterions!

Observations:
Pure Na system swell
Pure Ca system no swelling
Coexistence at intermediate mixing.
Generic behavior.



NaAOT - CaAOT-water

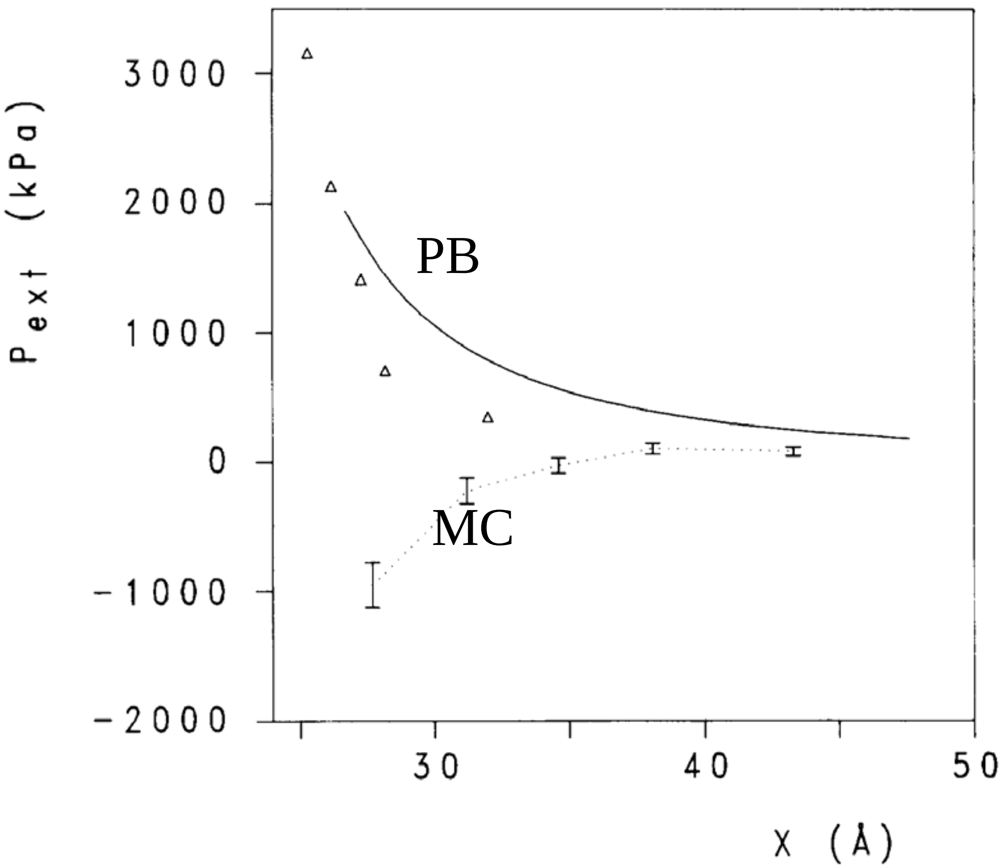
Khan,Jönsson,HW J.Phys.Chem 1985

Ion correlations 3

Q:Is geometry important for attraction?

A:MC simulation on DNA-like system.

Result:Attraction also in cylindrical systems.
Less pronounced.



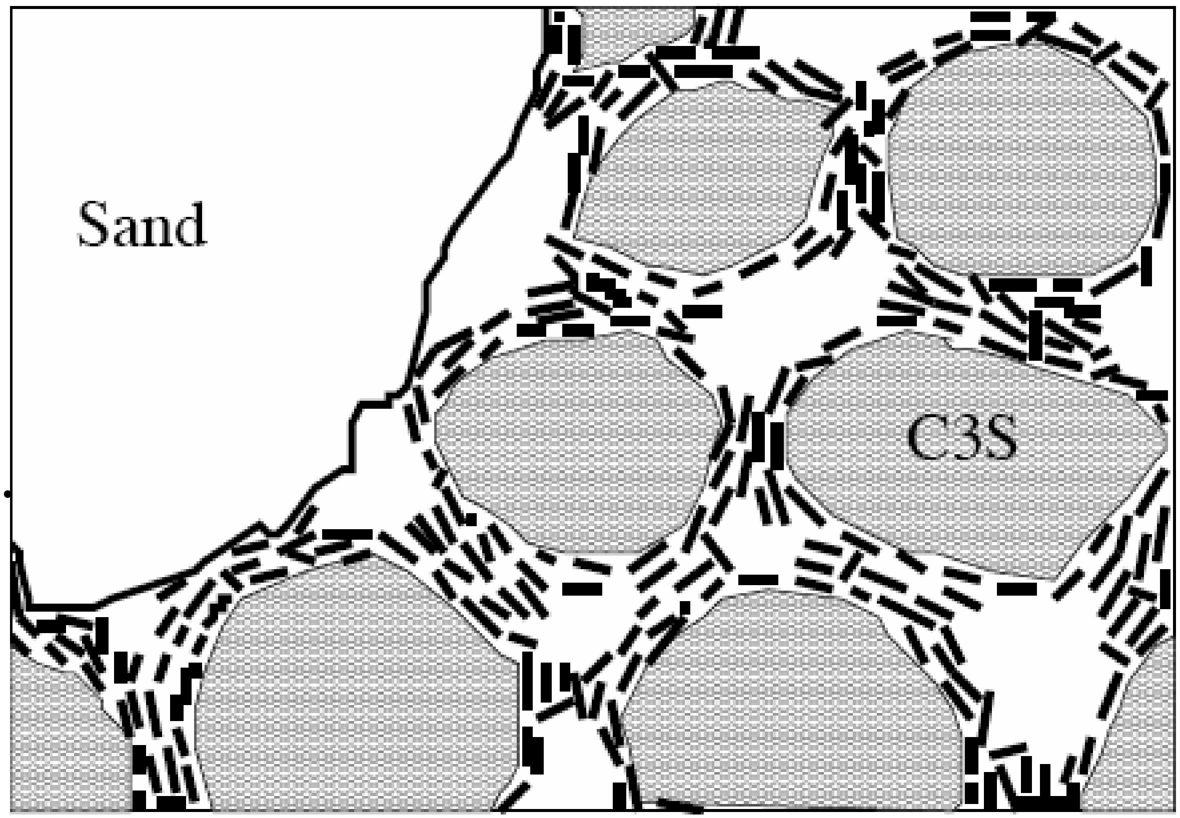
Guldbrand,Nilsson, Nordensköld, J.Chem.Phys 1986

Ion correlations 4

Q:Practical application of correlation attraction

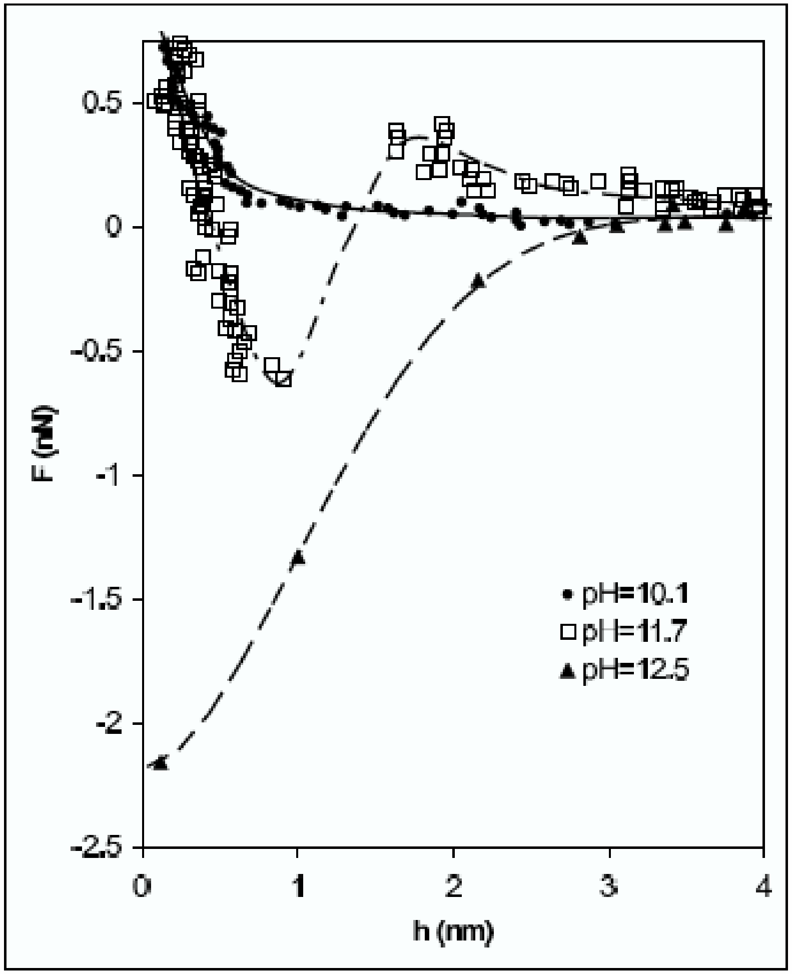
A:Cohesion in cement

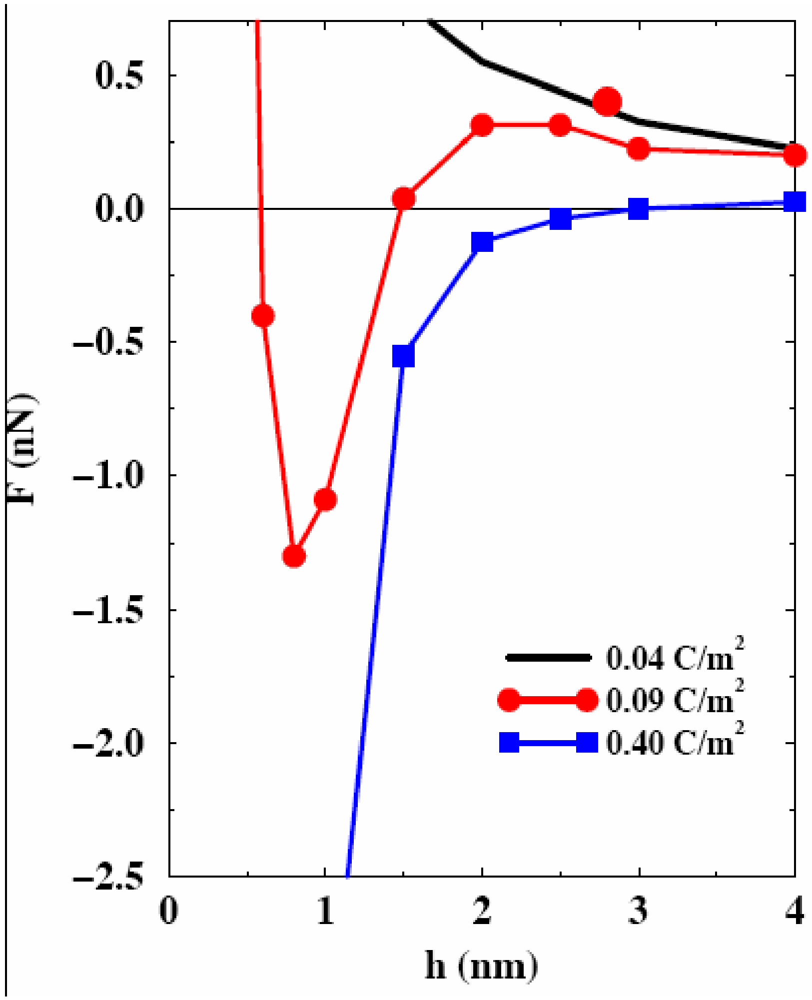
In wet cement “C3S” particles dissolve and charged silica-sulfate nanoparticles precipitate. pH increases steadily.



Jönsson,HW,Nonat,Cabane Langmuir 2004

Ion correlations 5





Measured interparticle force. AFM

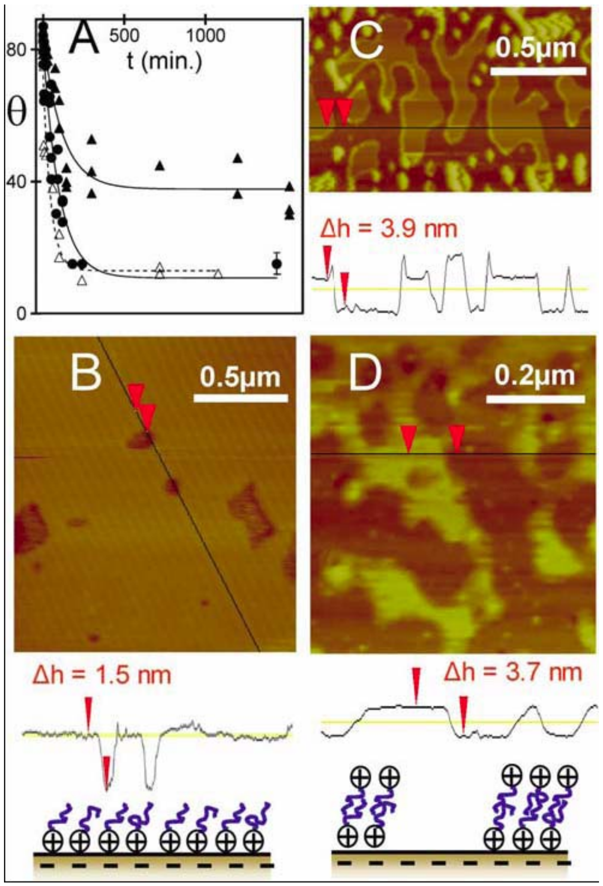
MC simulation for varying charge density.

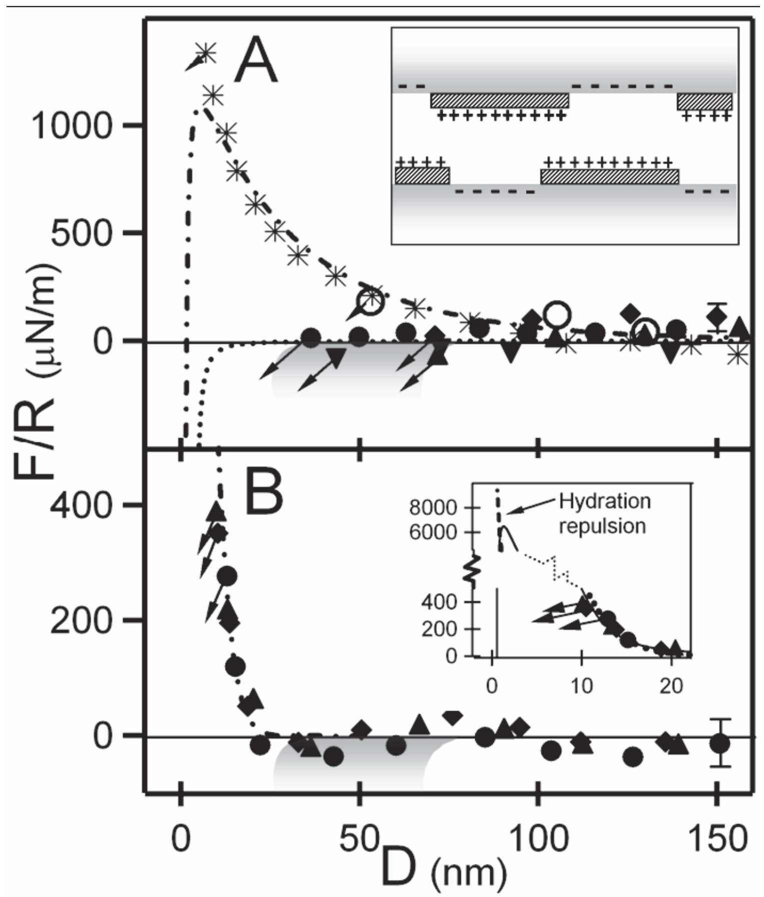
Jönsson,HW,Nonat,Cabane Langmuir 2004

Domain correlations

$$\frac{Force}{Area} \approx -\frac{\sigma^2}{2\varepsilon_r\varepsilon_0}\{\exp[(\kappa^2 + 3.4/R^2)^{1/2} h/2] + \exp[-(\kappa^2 + 3.4/R^2)^{1/2} h/2]\}^{-2}$$

Tsao,Evans,HW Science 1993





Attraction observed for patchy surfaces

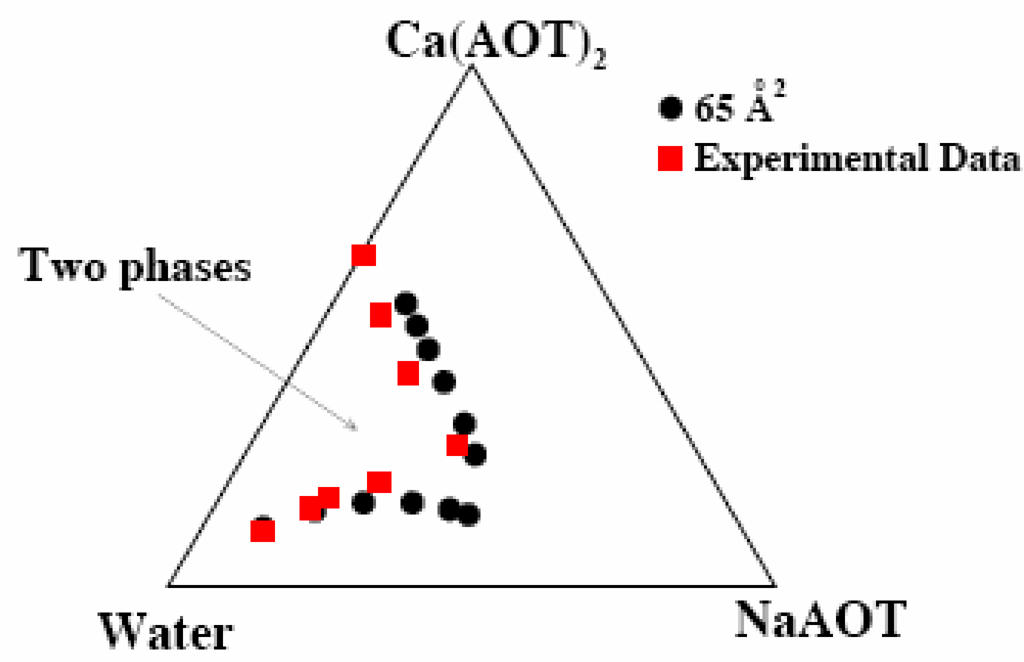
Perkin,Kampf,Klein Phys.Rev.Lett 2006

The dielectric approximation 1

Q:Accuracy of the dielectric model of water?

A:Quantitative test of MC simulations relative to experimental phase diagram.

Theory appears to work quantitatively even for separations of 1nm!?



Turesson,Forsman,Åkesson,Jönsson,Langmuir 2004

Khan,Jönsson,HW J.Phys.Chem 1985

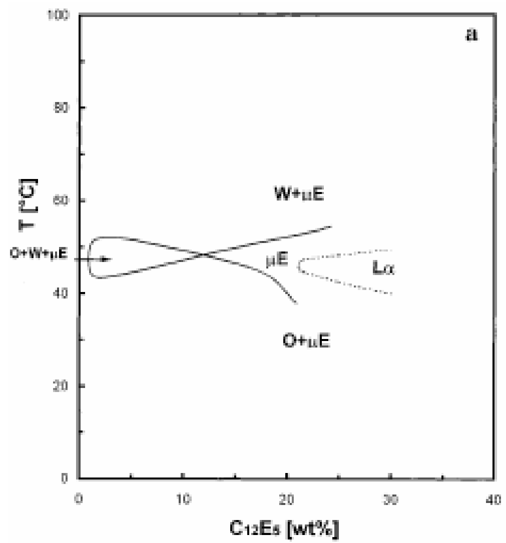
The dielectric approximation 2

Q:Temperature dependence of electrostatic interactions?

Observation:The dielectric permittivitty of water has anomalous T-dependence! Electrostatic free energy larger at high T.

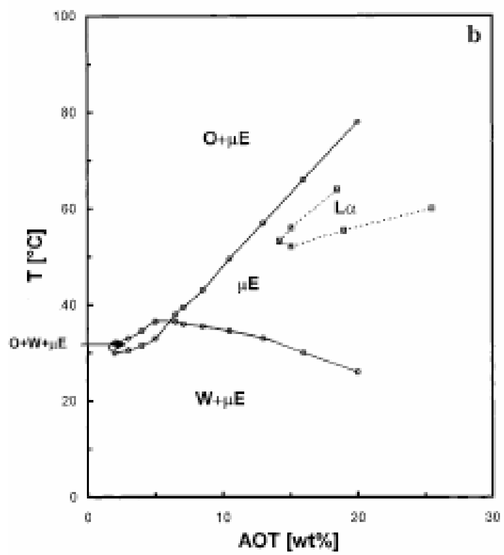
Test: Ionic microemulsions

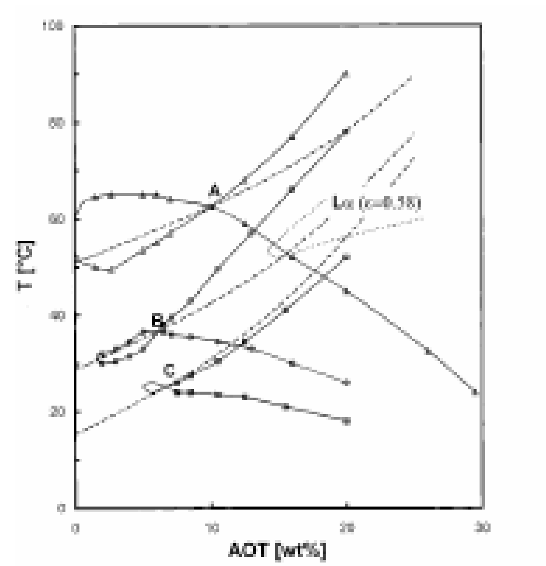
PB theory describes temperature dependence quantitativly!



Non-ionic system

Full lines:calculation based on PB equation and cell model





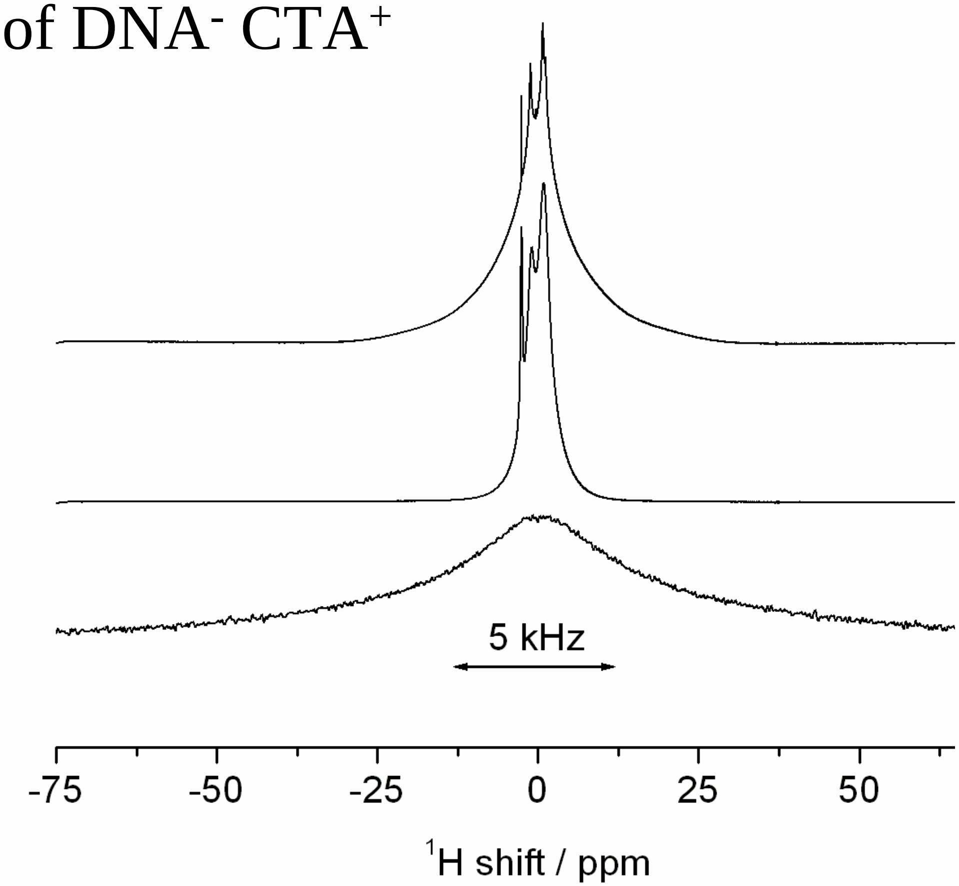
Carlsson,Fogden,HW Langmuir 1999

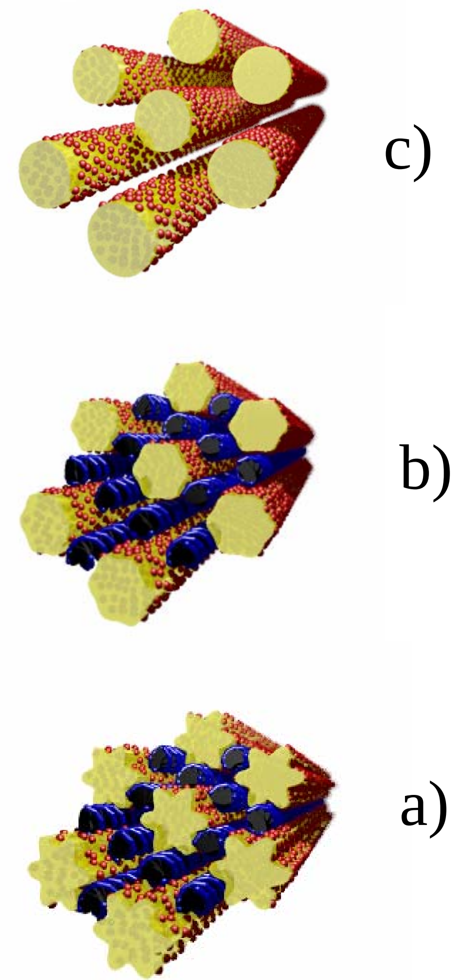
Ionic system

The dielectric approximation 3

Q:Attractive electrostatic interactions at short range?

A:Hydration of DNA^{-} CTA^{+}





Proton NMR,alkyl chain and CH_3

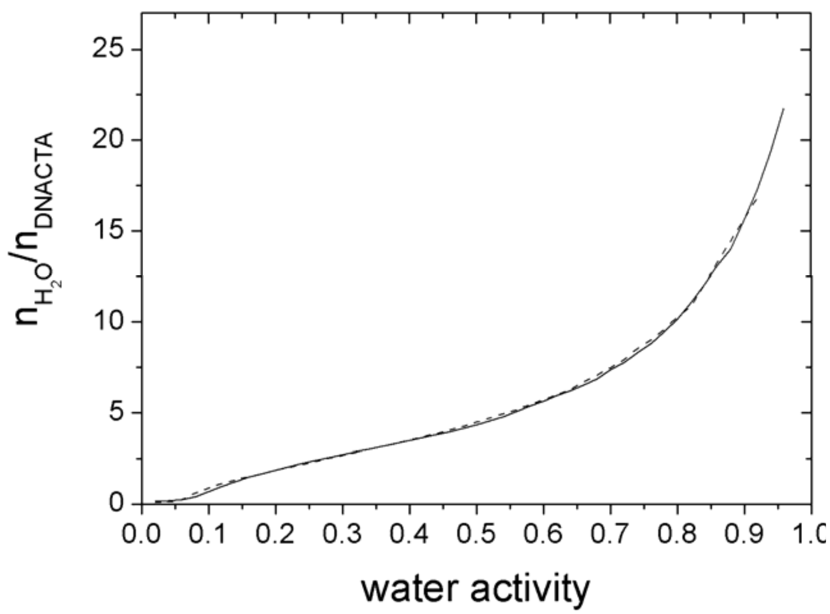
Leal,Topgaard,Martin,HW
J.Phys.Chem2004

The dielectric approximation 4

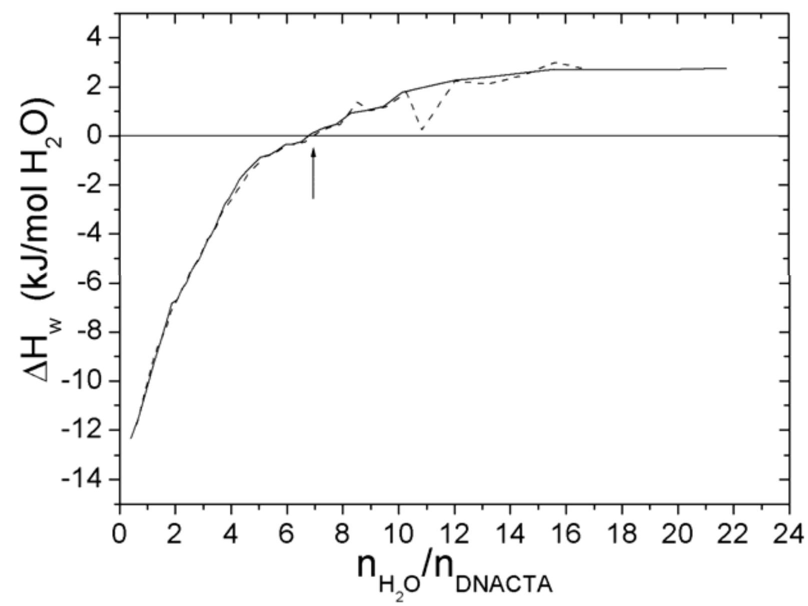
Q:Thermodynamics of hydration?

A:Calorimetric study of of DNA^{-} CTA^{+}

Free energy



Enthalpy

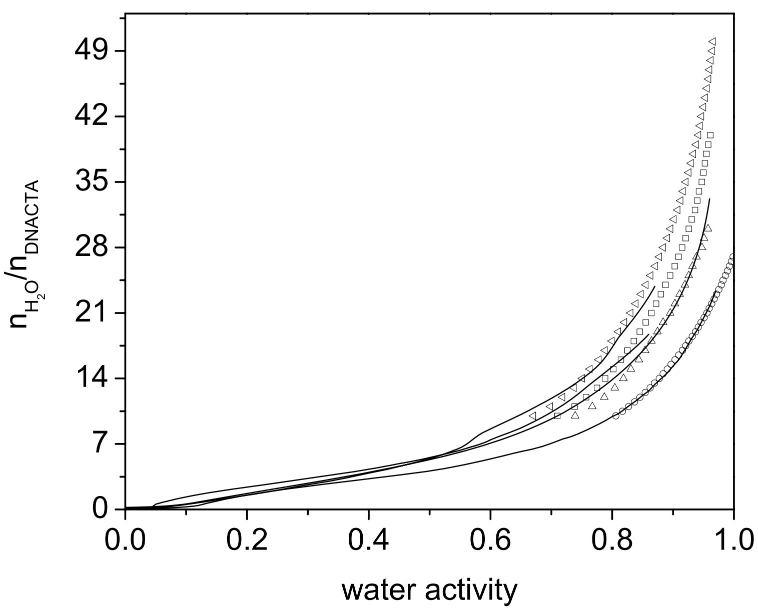


Leal,Wadsö,Olofsson,Miguel,HW J.Phys.Chem B 2004

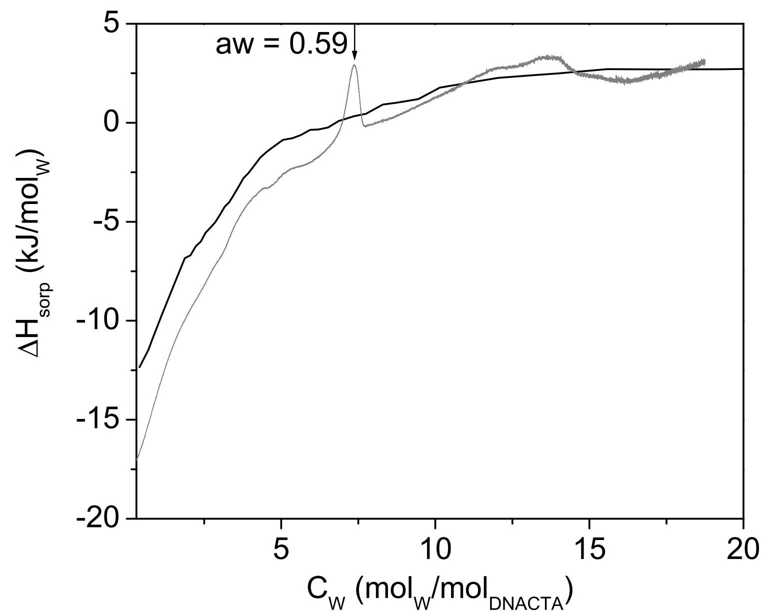
The dielectric approximation 5

Q:Effect of salt?

A:Add NaCl to dry DNA$^-$ CTA$^+$.



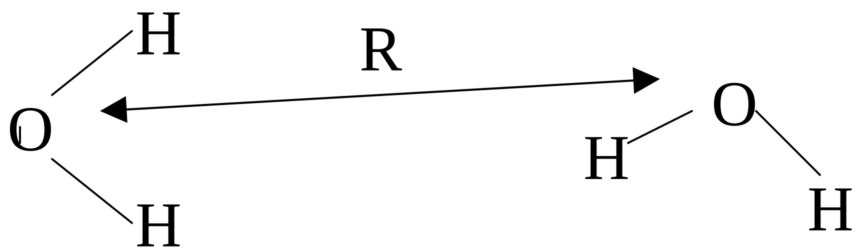
Dissolution of NaCl in complex



Result:Salt increases swelling. Effect can be modeled using PB equation

Leal,Moniri,Pegado,HW Submitted

Lifshitz theory and classical electrostatics 1



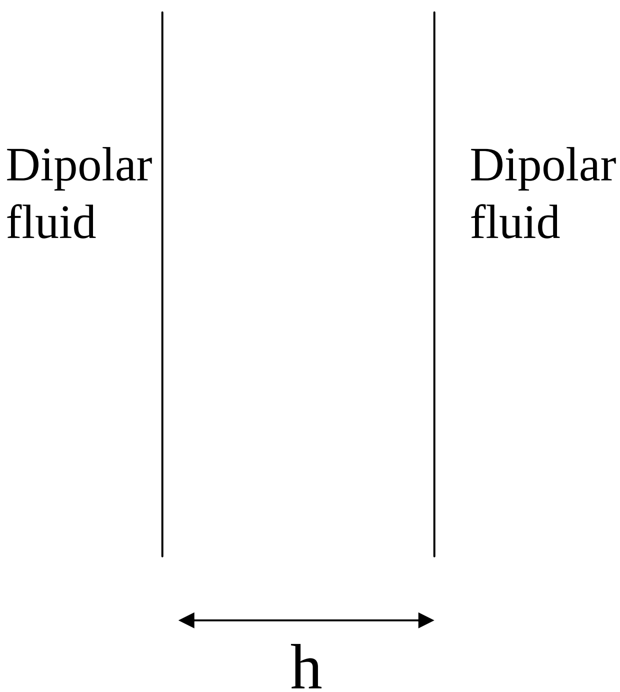
$$V(R) = -\frac{3kT\alpha^2}{(4\pi\varepsilon_0)^2 R^6}$$

Dispersion
Debye and
Keesom interactions
have an identical
asymptotic form for
the free energy!!!
(but for energy)

HW,Daicic,Ninham Phys.Rev.A 1999

Lifshitz theory and classical electrostatics 2

$$G/area = -\frac{kT}{32\pi h^2}\int_0^\infty x^2\{(\frac{\varepsilon(0)+1}{\varepsilon(0)-1})^2 e^x - 1\}^{-1}dx$$



Comment: An elementary use
of Lifshitz theory would suggest
a different expression!

HW Collids&Surfaces A 2003

Unresolved issues

The breakdown of the dielectric approximation
Interactions at short range, adhesion, binding constants
Anions at polar-apolar interface
The distance dependence of the hydrophobic interaction
Dipolar correlations in water
Classical-quantum high T free energy equivalence

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