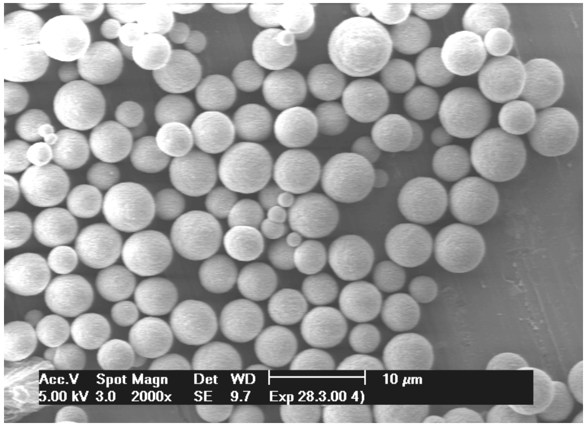
Week 9

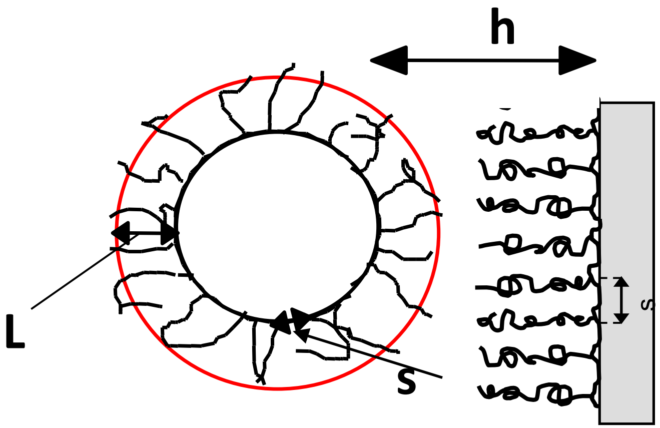
9. Powder Treatment (2)

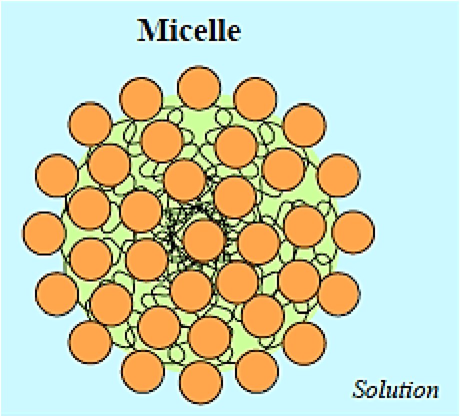
Part 1 -Polymers in solution: solubility, conformation, adsorption at interfaces, Steric stabilisation.

Part 2- Surfactants and micelles - colloids

A. Testino







The Colloidal Domain – D.F. Evans & H. Wennerström, Wiley, 1999. (Chp. 1,4 & 7)

Themes

- Other SMX Courses - Polymer Science
  - Frauenrath & Plummer
- Summary… of important concepts for colloids and steric stabilization
- Classification and Characteristics of Polymers
- Solubility of Polymers
- Conformations of Dissolved Polymers
- Dissolved Polymers at Interfaces
- Colloidal stability
- **This week** - exercises – ceramics – Open access program - HAMAKER

The Colloidal Domain – D.F. Evans & H. Wennerström, Wiley, 1999. (Chp. 7)

Summary

Polymers in solution and at interfaces

Classification and characteristics of polymers (5-9)
- chain structures (5)
- types of polymers (6-7)

Solubility of polymers (8-10)

Conformation of dissolved polymers (11-14)
- triangle by Haug (11)

Repulsive forces- stabilization steric (12-16)
- absorbed layer - repulsion (14-16)

Example polyacrylic acid and pastis (17-19)

Overall interaction energy (20-21)

Interparticle potentials – summary (22)

Assessment of colloidal stability (23-24)

Surfactants & Micelles (25-44)

Types of colloidal dispersions (26)

Topics (27)

Surfactants in everyday use (28)

Amphiphilic molecules (29-32)
- definition & examples (29)
- self assembly (30)
- micelle formation (31)
- solubility (32)

Micellar Association (33-39)
- association reaction, "close association" model (33-35)
- values of the CMC (36)
- detection of micellization (37)
- electrostatic effects on CMC (38-39)

Applications - Detergents (40-44)

Classification and Characteristics of Polymers

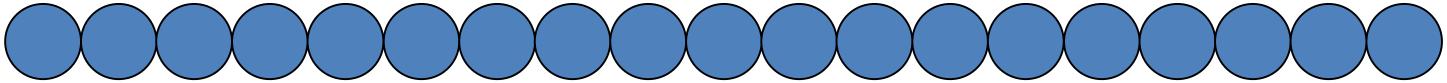
Polymer Types

❖ Homopolymers

Succession of N_M identical *monomers* (A) attached by *covalent* bonds : $\mathbf{(A)_n}$

$$M_P = N_M M_M = N_p M_M$$

M_P is the molar mass of the polymer; M_M is the molar mass of a *monomer*. N_p the degree of polymerization



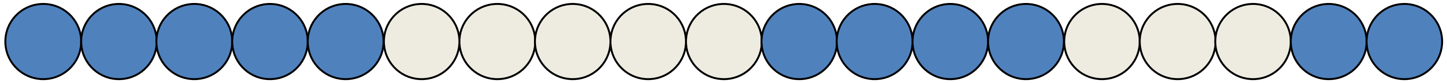
- ☞ Uniform interactions along the chain.
- ☞ Random conformation of the molecule.

❖ Block copolymers

Combinations of two or more homo-polymeric *chains* : $(A)_a$ - $(B)_b$

$$M_P = aM_A + bM_B$$

✓ **BLOCK COPOLYMERS:**



- ☞ Behavior similar to amphiphiles… surfactants.

https://polymerdatabase.com/main.html

TYPES OF POLYMERS

Heteropolymers

Random succession of two or more *monomers of a different* natures :

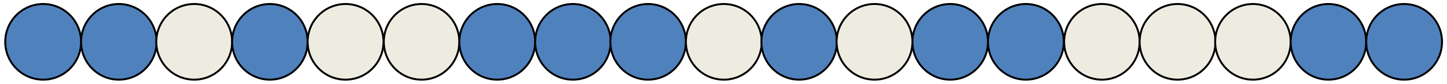
Example: DNA is a combination of four nucleotides

(Adenine, A; Guanine, G; Cytosine, C and Thymine, T)

$$M_P = aM_A + gM_G + cM_C + tM_T$$

...AGACACTGAAGGTCCGATG... = $A_aG_gC_cT_t$

✓ **HETEROPOLYMERS:**



☞ The conformation is determined by the sequence of the monomers.

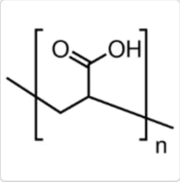
Example: Acrylonitrile/butadiene/styrene (ABS)

https://coolmag.net/polymeric-materials-for-automotive-applications/

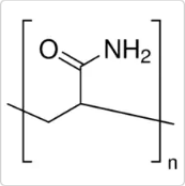
TYPES OF POLYMERS

Poly-electrolytes

The chain carries *ionizable* functional groups.

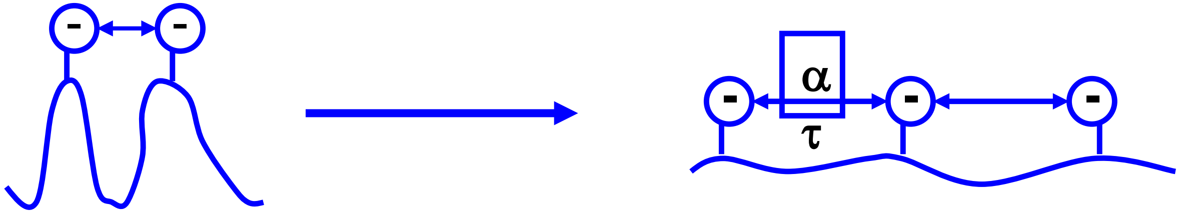


Examples: Poly (sodium acrylate) (PAA-Na): **$[–CH (COONa) –CH_2-]_n$**



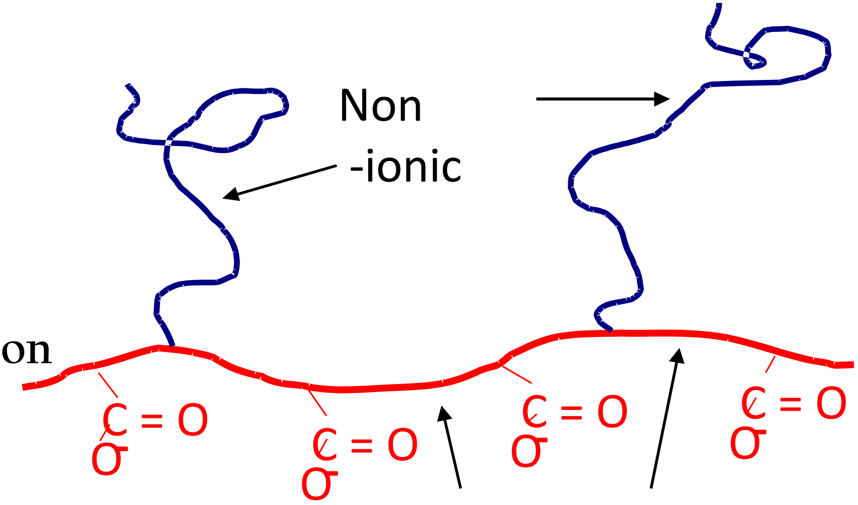
Poly (acrylamide): **$[–CH (CONH_2) –CH_2-]$**

- ✓ **POLYELECTROLYTES: if the monomers carry a charge**
- ✓ **Intramolecular repulsions tending to extend the chain**



- ✓**POLYELECTROLYTES - branched**
- ✓ :the monomers carry a charge
- ✓- Typical of polycarboxylate –

Superplacticizers used in cement dispersion



Anionic groups

Solubility of Polymers

Thermodynamics of polymer solutions

Free enthalpy of dissolution

- The free enthalpy of dissolution of a polymer comprises *three contributions* :
- ***interaction energy*** with solvent molecules - depends on w - the interaction parameter of the polymer with solvent.
- ***entropy of mixing*** with the molecules of the solvent (depends on n_p, number of moles of polymer);
- ***conformational entropy*** (depend on N_M, number of monomers ($=N_p$) and the flexibility of the chain).

Number of conformations

- A polymer chain in solution can adopt a large ***number of conformations*** Ω, which is a variable depending on N_M molar mass and ***flexibility*** of the chain.
- **Example:** for a polymer with a degree of polymerization $N_M = N_p = 1000$, in which two adjacent monomers can adopt 3 distinct orientations, we find:

$$\Omega \cong 3^{1000} \cong 10^{477} \quad (7.1.9)$$

Solubility of Polymers

Thermodynamics of polymer solutions

Probability of conformations

- The probabilities of the different configurations depend on the ***intrachain interactions*** **:**
- two monomers cannot simultaneously occupy the same space **-** ***excluded volume***
- they can repel or attract each other **(*Coulomb interactions*** in the **polyelectrolytes**, e.g. proteins) ;
- they can ***interact*** with the ***solvent*** molecules.
- Locally, the polymer finds itself as in a mixture of liquids (cf. Ch. 3 Colloidal Domain), characterized by the interaction parameter w.
- The theory of mixtures can be applied to the case of polymer solutions, provided that the coordination number is redefined z_b, because each monomer is attached to their neighbours by *covalent bonds*.

Solubility of Polymers

Thermodynamics of polymer solutions

- Solvent quality. χ *parameter*
- χ (chi) characterizes the interaction between solvent and the dissolved polymer chain.

By definition : $$\chi = \frac{w}{RT} \qquad (7.1.10)$$

.. or empirical eqs:
$\chi(T) = A + B/T + C/T^2$

- Three possible cases can arise::

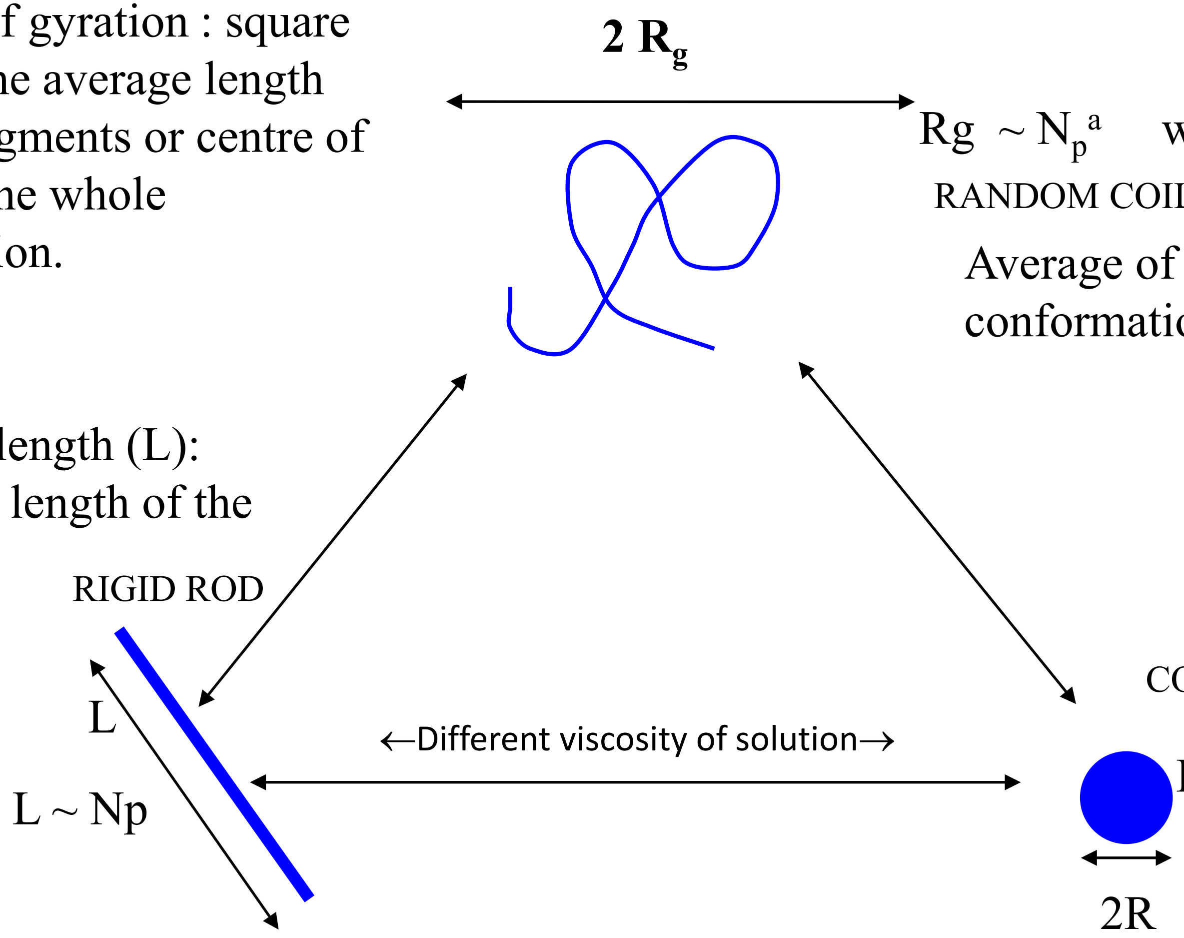
- $\chi < 1/2$:
- weak intra-chain attractions → The configuration of the dissolved polymer is dominated by *entropy* (*GOOD* solvent).

- $\chi > 1/2$:
- strong monomer-solvent repulsion → The structure of the chain is determined by the *interactions* between *monomers* (*POOR* solvent).

- $\chi = 1/2$:
- transition between *good* and *poor* solvent → This transition takes place at a temperature $T = \theta$ characteristic of the type of polymer and solvent *(θ solvent)*.

CONFORMATION OF POLYMERS

Radius of gyration : square root of the average length of the segments or centre of gravity the whole distribution.



$2\ R_g$

$Rg \sim N_p^a$ with $0,5 < a < 1$

RANDOM COIL

Average of a lot of possible conformations

Stretched length (L): developed length of the chain

RIGID ROD

L

$L \sim Np$

←Different viscosity of solution→

COMPACT GLOBULE

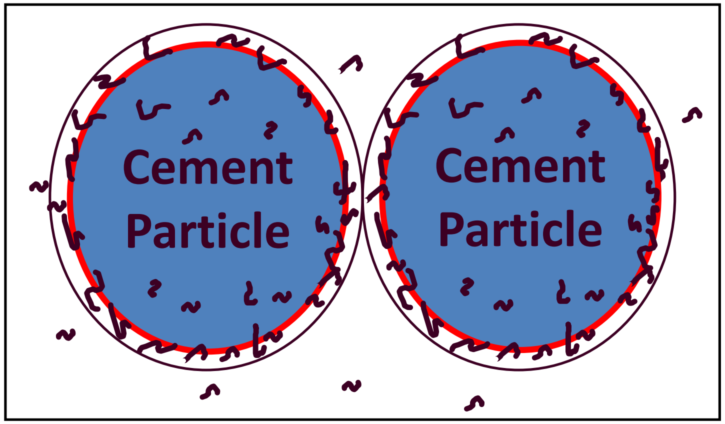
$R \sim Np^{0,3}$

2R

The solvent /monomer interactions play an important role in the solvent's quality for large N_p:

In poor solvent: $R_g \approx N^{0,3} \approx M^{0,3}$ In good solvent: $R_g \approx N^{0,6} \approx M^{0,6}$

Repulsive forces - steric stabilization *



Stabilization requires adsorption:

Depends on 3 interactions:

1. polymer - polymer,
2. polymer - solvent and
3. polymer - particle

- That is to say - the relative affinity of the solvent and the polymer for the surface of the ceramic powder.
- Need a good surface coverage and coverage remains constant during the close approach (collision) of the particles
- Adsorption needs to be strong enough that polymer does not desorb due to high shear forces during shaping (wet shaping techniques)
- Polymer must also have an affinity for the solvent.
- So that the polymer can extend into the solution in order to develop a good steric repulsion

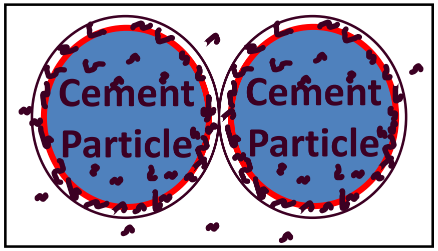
*Chp.2.4.3.3 (p158-167), Les Traité des Matériaux, Vol.16 «Les Céramiques »

J. Barton, P. Bowen, C. Carry & J.M. Haussonne, PPUR, 2005

Adsorbed layer - repulsion

- Repulsion is felt when the polymer layers overlap

- The more these layers are extended the sooner the repulsion is felt and therefore the effect of the attractive van der Waals forces will be limited.

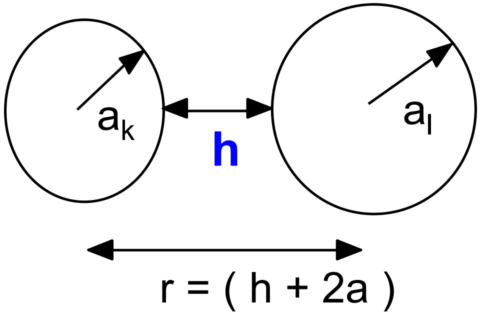


Theoretical approach

- Both enthalpy and entropy contribute to the force of repulsion.

Enthalpic

- an interpenetration of the polymers reduces the contact between the solvent and the polymeric chains (due to polymer-polymer contact).
- this changes the mixing enthalpy of the system giving our input enthalpy. (concentration gradient between bulk and interparticle space – osmotic pressure pushes particles apart)



Entropic

- as the adsorbed layer approach, each polymer can no longer adopt as many configurations as before – loss of disorder higher free energy – repulsion to avoid this – giving a repulsive entropic contribution.

Interaction between flat surfaces covered with polymers

Depends on polymer-solvent-particle interactions & particle geometry

- High density of adsorbed polymer
- The attached polymer chains can form a *brush structure*.
- In a good solvent, the interaction pressure (F/A) between **flat surfaces**,
- for nonionic block polymers, using a statistical mechanics approach*, is given by:

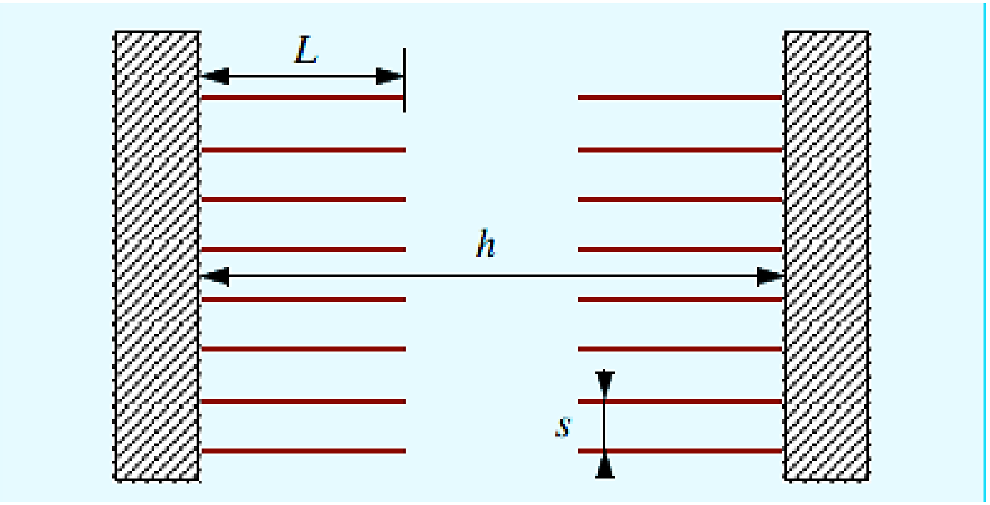
$$\frac{F}{A} = const\,\frac{kT}{s^3}\left(\frac{2L}{h}\right)^{9/4}\left[1-\left(\frac{h}{2L}\right)^3\right] \quad ; h \leq 2L \quad (7.4.2)$$

where

L is the adsorbed layer *thickness*,

h the *separation* distance between surfaces

s the distance *lateral* separation between ch



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*Shlomo and de Gennes Advances in Colloid and Interfaces Science, **27**, 1987, 189-209

2

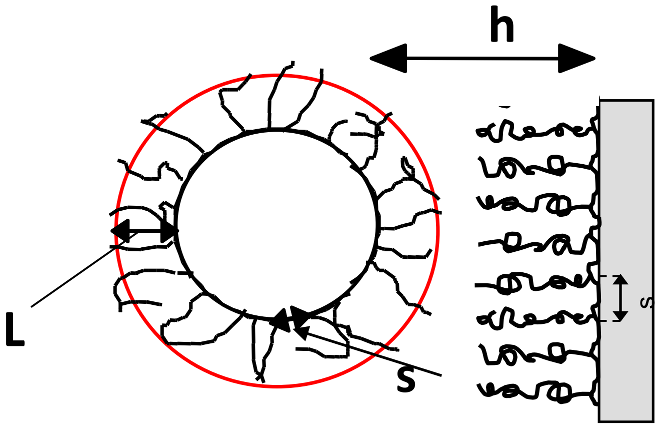
Interaction between polymer layers - plate - sphere (AFM)

Depends on polymer-solvent-particle interactions & particle geometry

- High density of adsorbed polymer (in a good solvent)
- The attached polymer chains can form a *brush structure*.
- Expressions - geometry specific - **plate/sphere** - AFM- brushes

$$F_s = \frac{8\pi kT}{35}\frac{aL}{s^3}\left[7\left(\frac{2L}{h}\right) + 5\left(\frac{h}{2L}\right)^{7/4} - 12\right]$$ Eq. 2.67 (b)

a the radius of a sphere,
h distance between particle surfaces.
s is the distance between the points of adsorption of the polymer chains,
L is the thickness of the polymer layer,



*Shlomo and de Gennes Advances in Colloid and Interfaces Science, **27**, 1987, 189-209)

Interaction between polymer layers – sphere–sphere - mushrooms

2

$$F_{ster}\left(a_k, a_l\right) = 2\pi \bar{a} \frac{3}{5} \frac{k_B T}{s^2}\left[\left(\frac{2L}{h}\right)^{5/3} - 1\right]$$

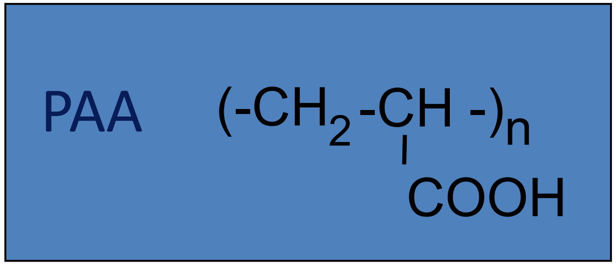
L - Adsorbed layer thickness
s - Spacing of adsorbed molecules
Sphere-sphere geometry

Harmonic average radius

$$\bar{a} = \frac{2a_k a_l}{a_k + a_l}$$

P.G. de Gennes Advances in Colloid and Interfaces Science, **27**, 1987, 189-209.,
Image – R. Flatt Thesis EPFL no. 2040 (1999)

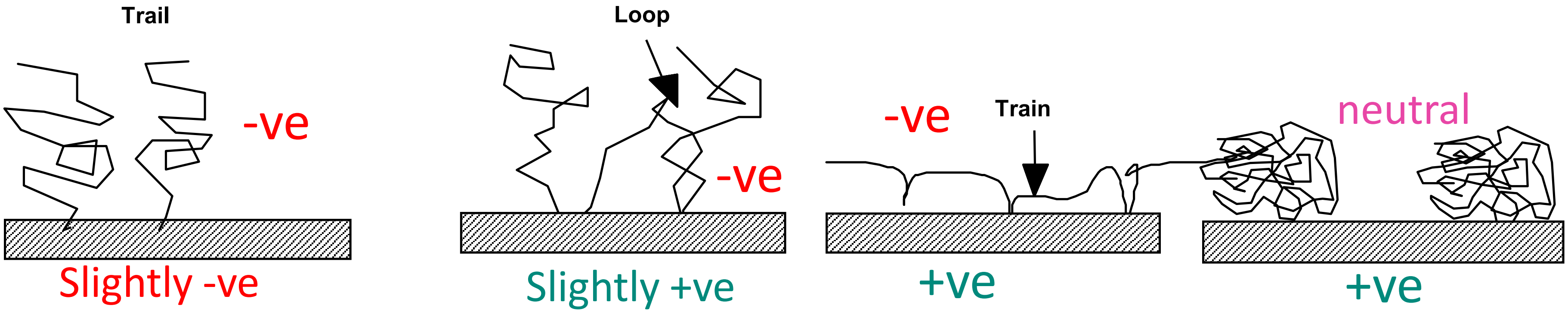
Polymer conformation - Polyacrylic Acid on Alumina



$$\text{PAA}\qquad (-CH_2-\underset{\substack{|\\ COOH}}{CH}-)_n$$

Example: polymer conformation

- Adsorption of polyacrylic acid on alumina (Al_2O_3)
- Isoelectric point - Al_2O_3, pH = 9,
- PAA fully dissociated for pH> 6
- Adsorbed layer thickness can be measured by Atomic Force Microscopy – AFM*
- Or from atomistic modelling$
- Steric and electrostatic contributions from carboxylate groups – electro-steric stabilization



PAA - pH > 11

brush

PAA - pH = 8

mushroom

PAA - pH = 6

pancake

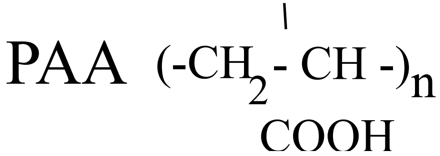
PAA - pH = 2

blob

- *M. Palacios, P. Bowen , M. Kappl, HJ. Butt, M. Stuer, C. Pecharromán, U. Aschauer, F. Puertas “Repulsion Forces of Superplasticizers on Alkali Activated Slag Pastes” Materiales de Construcción, 489-513, 62 (308), 2012
- $U. Aschauer et al ”,J.Coll.Inter.Sci. 346 (2010) 226–231

Adsorption conformation - "good" solvent

- Amount of PAA adsorbed on $BaTiO_3$ - 10 x higher at pH 1.5 cf pH 10
- But not stable - COOH not dissociated - water poor solvent



PAA $(\text{-CH}_2\text{- }\underset{\text{COOH}}{\text{CH}}\text{ -})_n$

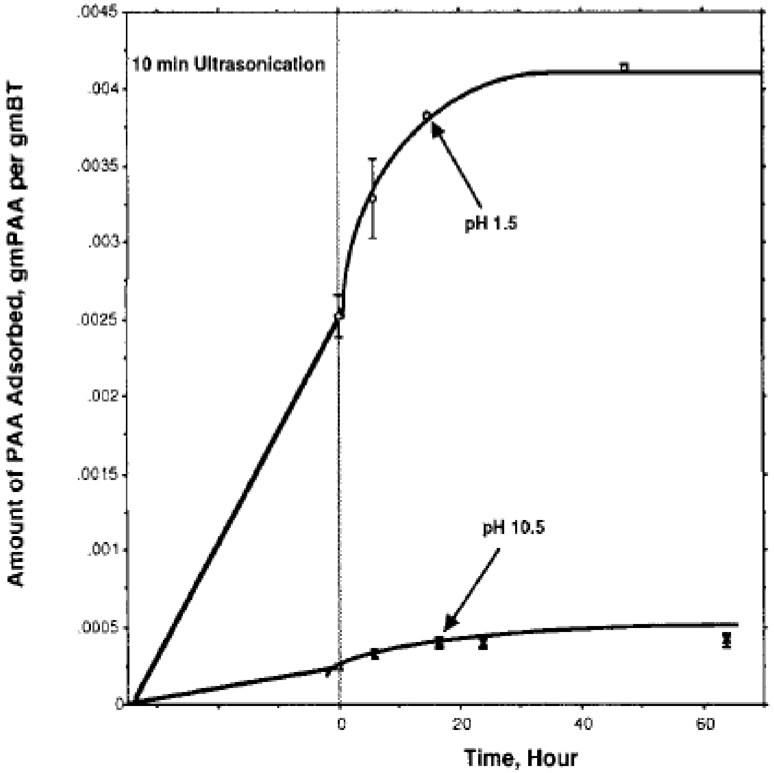


Fig. 5. Adsorption kinetics of PAA on $BaTiO_3$ surface at two different pH values. Solid volume fractions, *f*, of 14.23 and 6.23 vol% were performed for pH 10.5 and 1.5, respectively.

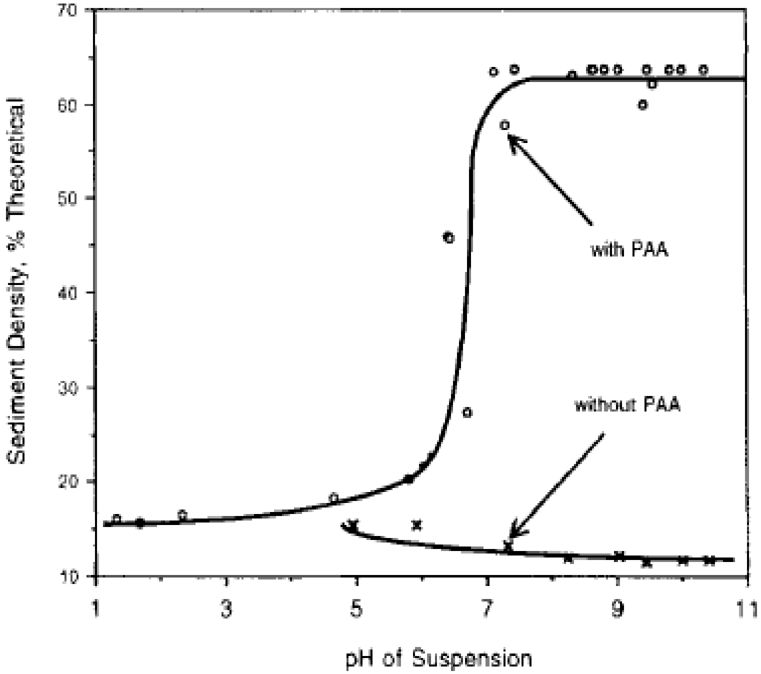


Fig. 8. Sediment density as a function of suspension pH. For the suspension with PAA, 14.24 vol% of solid was used, while 6.23 vol% of solid content was used for suspension without PAA.

Chen ZC, Ring TA, Lemaître J. J. Am. Ceram .. Soc. 75 (12) 3201-208 (1992)

Interparticle Forces - Hamaker*

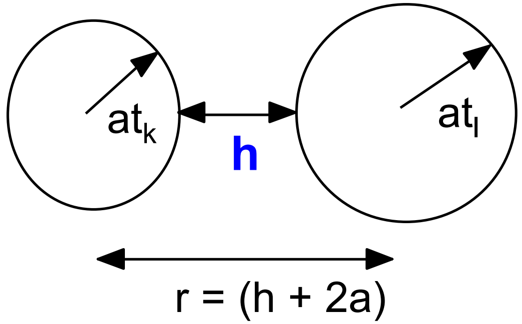
3

- **Attractive** - Van der gold dispersion Waals forces - A (h) - Hamaker constant (dielectric properties)

$$F_{(a_k,a_l,h)} \cong -A_{(h)} \frac{\bar{a}}{12h^2}$$

Harmonic average radius

$$\bar{a} = \frac{2a_k a_l}{a_k + a_l}$$



- **Repulsive**

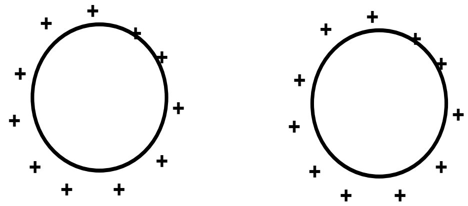
Electrostatic, ion adsorption, dissociation, polyelectrolyte

$$F_{ES} = -2\pi\varepsilon\varepsilon_0 a\psi^2 \frac{\kappa e^{-\kappa(h-2L)}}{\left(1+e^{-\kappa(h-2L)}\right)}$$

ψ Electrostatic potential From zeta potential)

$1/\kappa$– Electrical double layer thickness

L - load /zeta plane

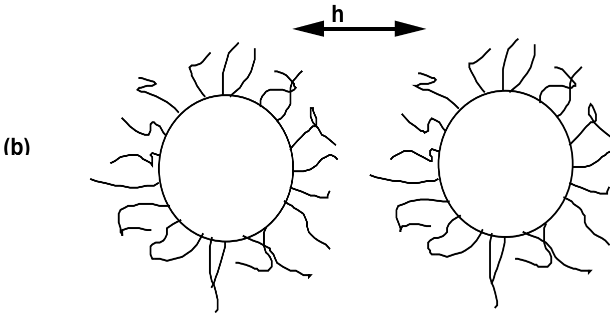


Steric -polymer adsorption - layer thickness

$$F_{ster}(a_k,a_l) = 2\pi a \frac{3}{5}\frac{k_B T}{s^2}\left[\left(\frac{2L_{ads}}{h}\right)^{5/3} - 1\right]$$

L_{ads} - Adsorbed layer thickness, s - Spacing of adsorbed molecules

In mushroom configuration - important geometry



(distance h between particles)

* U. Aschauer,et al J. Dispersion Science Technology, 32 (4), 470-479 (2011).

Overall Interaction Energy - Colloidal Stability

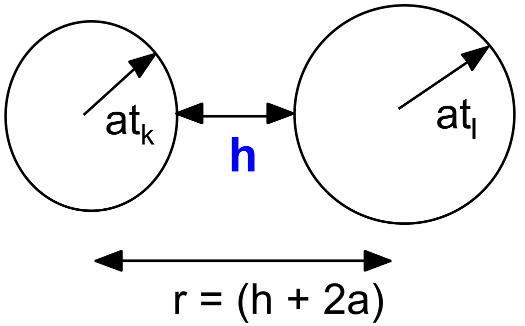
- Net potential/force is algebraic sum of repulsive and attractive forces… DLVO
- Size distributions taken into account*

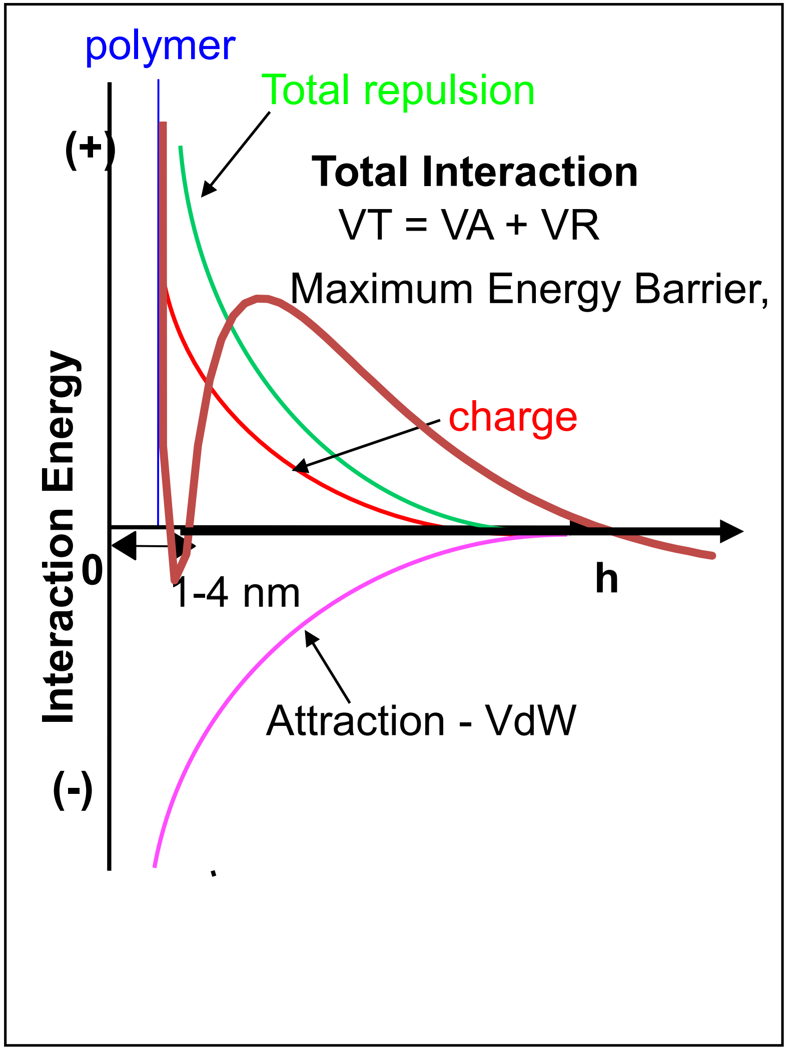
$$V_T = V_A + V_E \; (+ \; V_S)$$

$$F_{total(\bar{a}_h, h)} \cong F_{VdW} + F_{ES} + F_{Ster}$$

Harmonic average radius

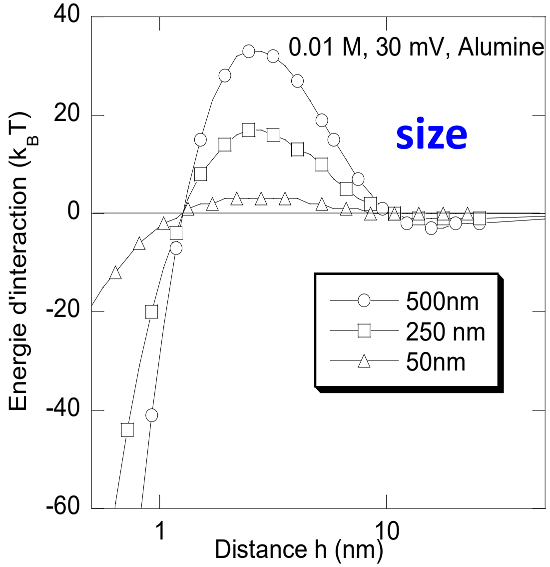
$$\bar{a} = \frac{2a_k a_l}{a_k + a_l}$$

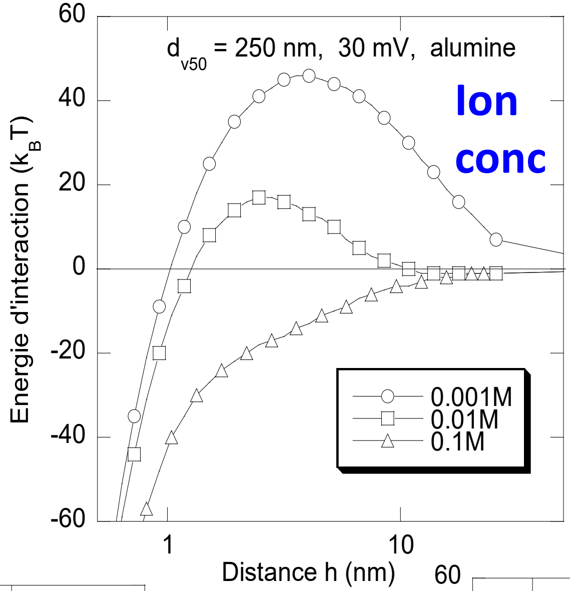


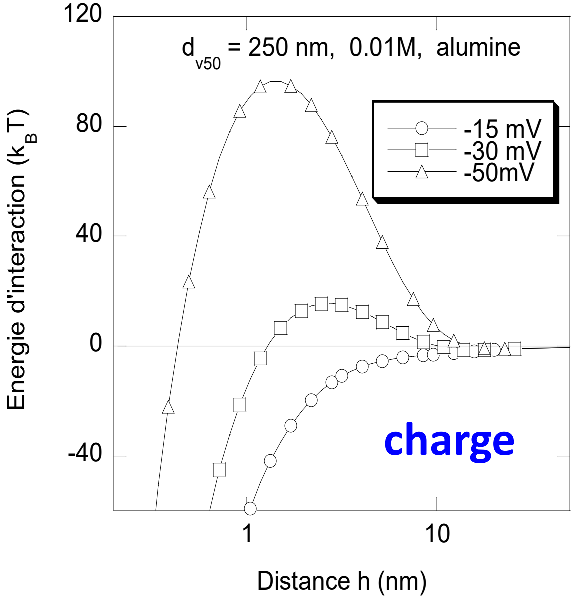


[#] Robert J. Flatt, Paul Bowen, J. Am. Ceram. Soc., 89 [4] 1244–1256 (2006)

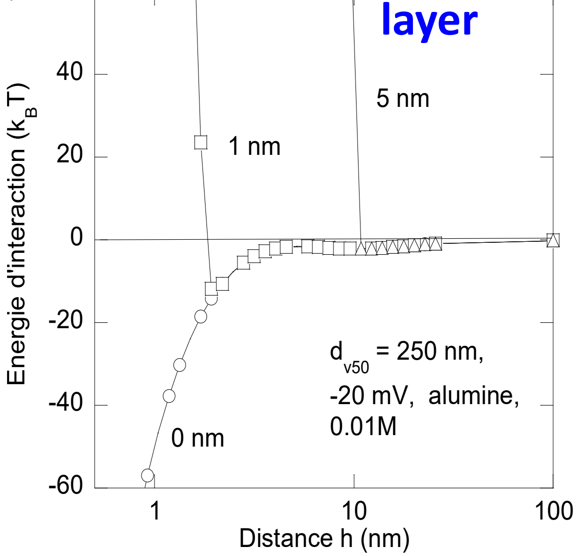
Interparticle potentials – summary - calculations – α Al2O3







Adsorbed layer



Assessment of colloidal stability

The examples above demonstrate

- It is difficult to generalize the type of potential barrier that can stabilize a ceramic dispersion.
- A calculation of the interactions at play can clearly improve the understanding and the choice of a dispersing system.
- The development of computers greatly facilitates the use of this approach without having to resort to too simplistic modeling of the phenomena.
- Few studies correctly predict the order of magnitude of interaction potentials and the same for rheology – yield stress and viscosity.
- Qualitative agreement generally good, but difficult to quantify…

There are several reasons for this

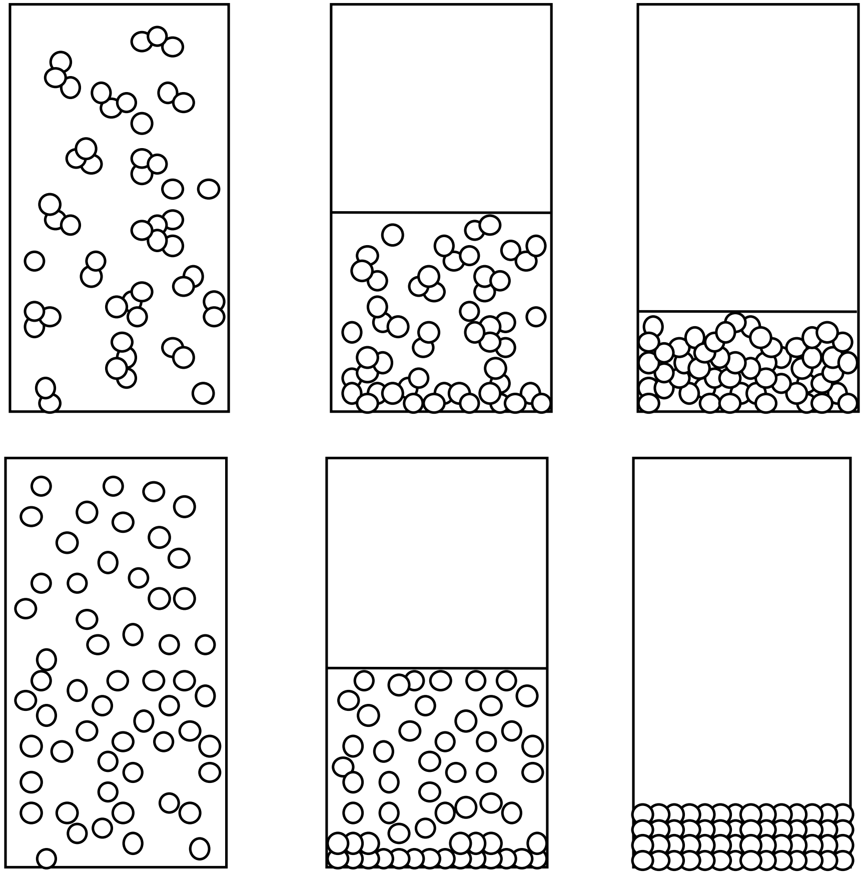
  - assumption of spherical particles and identical sizes
  - adsorbed layer thickness and conformation of the polymer (simulation , AFM)
  - unknown Hamaker constants,
  - hydrodynamic effects - soap in the bath!

- Facilitated by development of open access programs - e.g. *http://hamaker.epfl.ch*
- Exercises 9….we can test it out….

Assessment of dispersion

- Measure size distributions – smaller size better dispersion
- Rheology - more fluid lower viscosity - better dispersion
- Sedimentation volume - lower volume better dispersion
- Green body density – higher density better packing – better dispersion – higher final density after sintering!

Poorly dispersed - fast network formation
- low green density (30%)



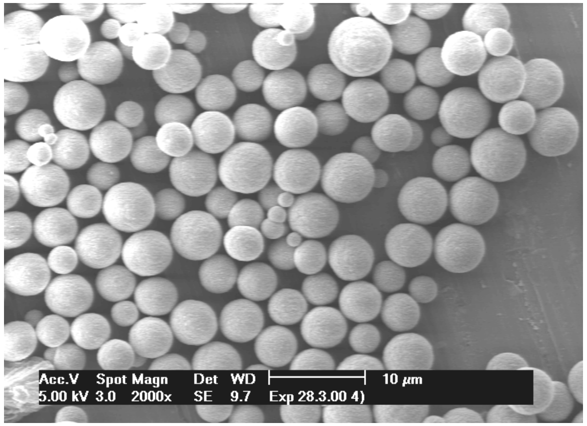
Well dispersed
- slow network formation
- high green density (70%)

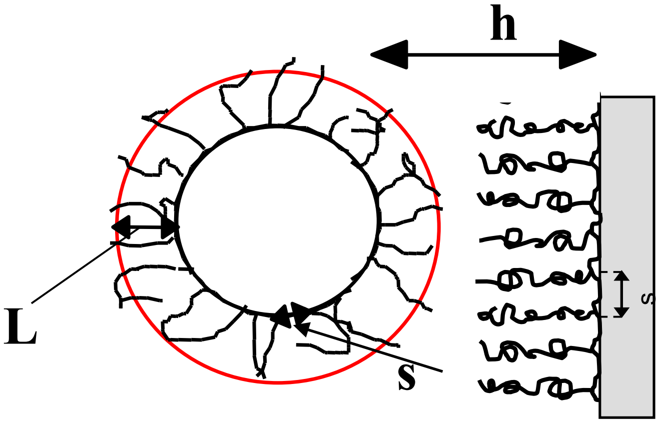
Week 9

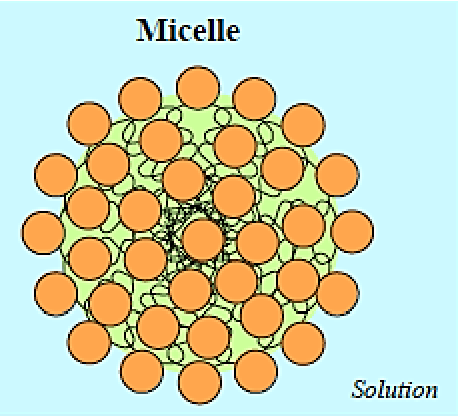
9. Powder Treatment (2)

Part 2- Surfactants and micelles - colloids

A. Testino







The Colloidal Domain – D.F. Evans & H. Wennerström, Wiley, 1999. (Chp. 1 & 4)

Types of colloidal dispersions

http://www.chemistrylearning.com/colloidal-dispersions/

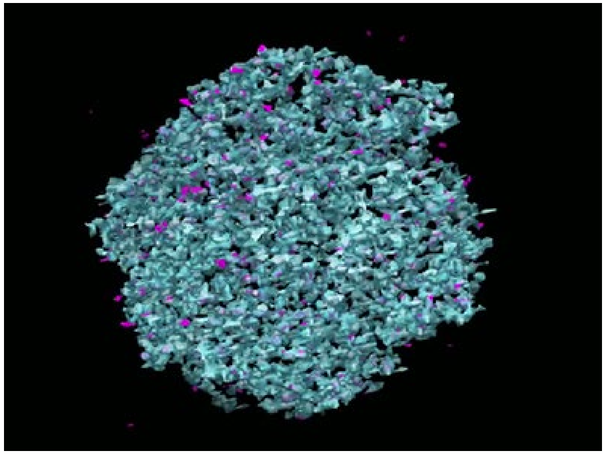
Dispersed Phase	**Dispersion Medium**	**Type of Colloidal Dispersions**	**Examples**
Gas	Liquid	Foam	Soap, beer, lemonade
Gas	Solid	Solid foam	Pumice stone
Gas	Gas	Does not exist	---
Liquid	Gas	Liquid Aerosol	Fog
Liquid	Liquid	Emulsions	Milk *, rubber
Liquid	Solid	Gel	Butter, Cheese
Solid	Gas	Solid Aerosol	Dust
Solid	Liquid	Sol or Colloidal Suspension	Paste, ink
Solid	Solid	Solid sol (solid suspension)	Pearls gem stones

* Holt C. Structure and stability of bovine casein micelles. Adv. Protein Chem. 1992; 43: 63–151.

Topics - Surfactants - Micelles

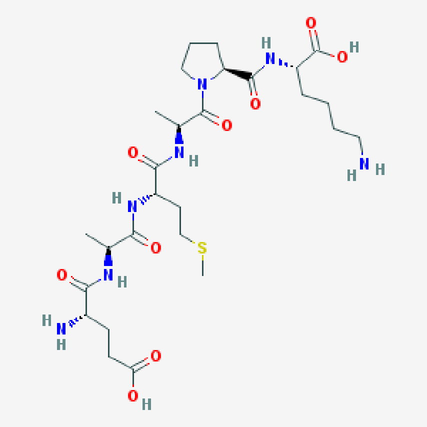
- Amphiphilic Molecules
  - Definition. Examples
  - Self-assembly
  - Micelle formation
  - Solubility
- Micellar Association
  - Association reaction
  - Formation of ionic micelles
  - Enthalpy and entropy of micellization
  - Detection of micellization
- Energetics of Micellar Solutions
  - Energy components of micellization
  - Ionic micellar solutions
  - Effect of electrostatic interactions on *CMC*
- Application
  - Detergents

casein micelle in milk



https://ag.tennessee.edu/news/Pages/3T-08harte-13.aspx

β-casein molecule (milk protein)



https://pubchem.ncbi.nlm.nih.gov/compound/14389255

Surfactants – in everyday use

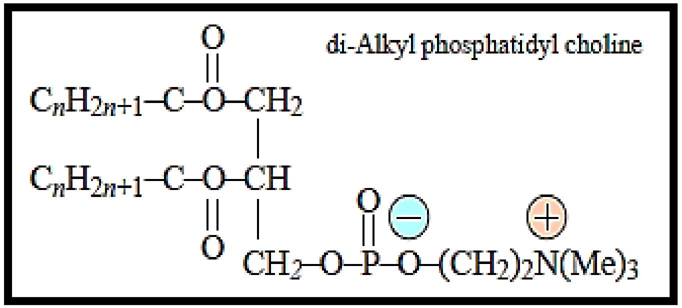
Amphiphilic Molecules - Definition & Examples

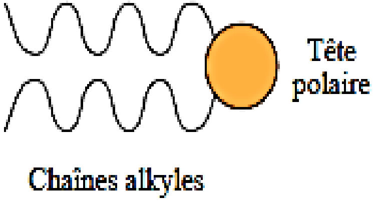
Definition: Surfactant

- *Amphiphilic* molecules (a.k.a. *surfactants*) present *simultaneously* a chemical affinity for polar liquids (*water*) and non-polar (*oil*).
- The amphiphilic character results from a particular chemical structure, generally associating one or more non-polar organic chains (*alkyl* chains) and a polar or ionized "head".

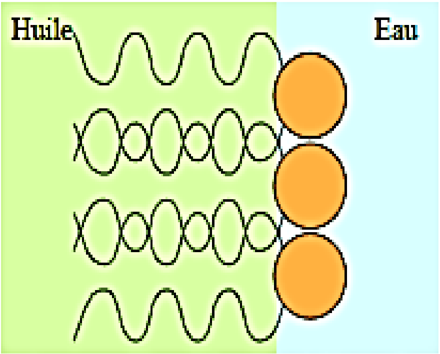
Surfactant properties

- In aqueous solution, surfactants *adsorb* spontaneously to the water-air or water-oil *interfaces*.
- The molecules of a surfactant adsorb so as to immerse their polar section in the aqueous medium, while their alkyl chains are excluded and are accommodated in the non-polar medium .





Structure d'une molécule amphiphile

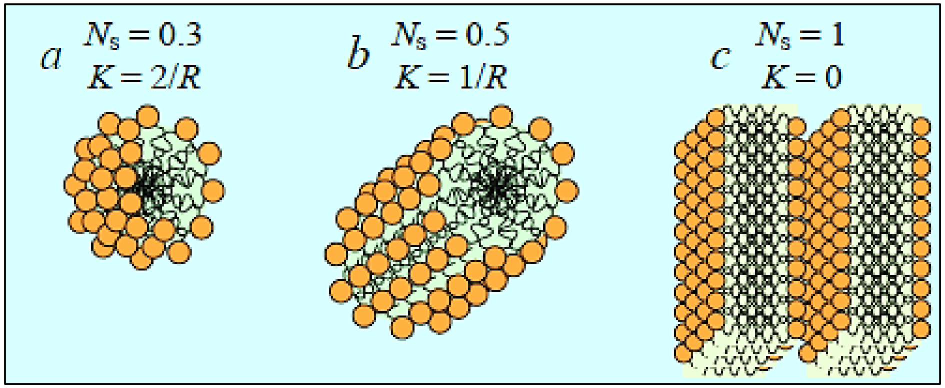


Adsorption de surfactants à l'interface eau-huile

Nom	Formule chimique	Type
Alkyl-carboxylate de Na	$C_nH_{2n+1}-CO_2-Na$	Anionique
Akyl-méthyl ammonium bromure	$C_nH_{2n+1}-N(Me)_3-Br$	Cationique
Di-alkyl phosphatidyl choline	(voir figure)	Zwitterionique
Alkyléthylène glycol	$C_nH_{2n+1}(OCH_2CH_2)_mOH$	Non-ionique

Exemples de surfactants

Amphiphilic Molecules - Self-assembly



Self-assembly modes

- Spherical micelle (*a*)
- Tubes (*b*)
- Films - bi-layers (*c*)

Surfactant index N_s

- The *mode of* self-assembly depends on
  - the *geometry of the* surfactant, characterized by an index N_s:

$$N_S = \frac{v}{l \cdot a_O} \qquad (1.3.1)$$

ν is the ***volume*** the alkyl chain, ***l*** its ***length***,

a_o [nm^2] the cross ***sectional area*** of the polar head.

- We can calculate ν and *l* from the characteristics of the alkyl chain:

$$v[nm^3] = 0.027(n_C + n_{Me}) \qquad (1.3.2)$$

$$l[nm] = 0.15 + 0.127 n_C \qquad (1.3.3)$$

- where n_c is the number of carbon in the chain and n_{Me} the number of methyl groups (including terminal methyls).

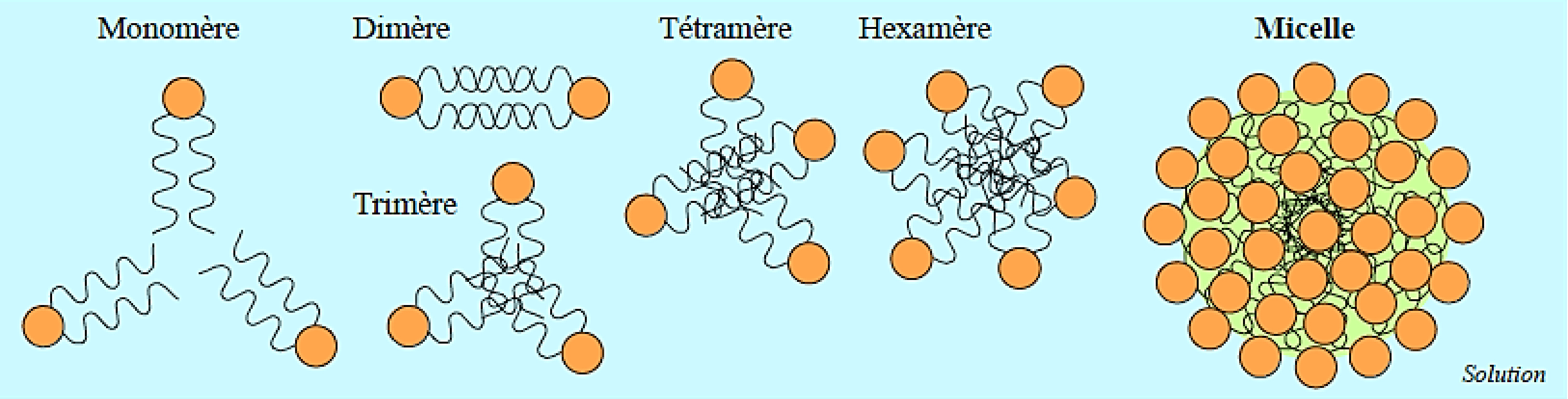
Amphiphilic Molecules - Micelle formation

Spontaneous appearance of micelles

- Micelles appear spontaneously in a solution as soon as the concentration of surfactant is greater than the **Critical Micellar Concentration (*CMC*).**
- This appearance influences the evolution of the surface tension of the solution (next slide).

Aggregation Number *NA*

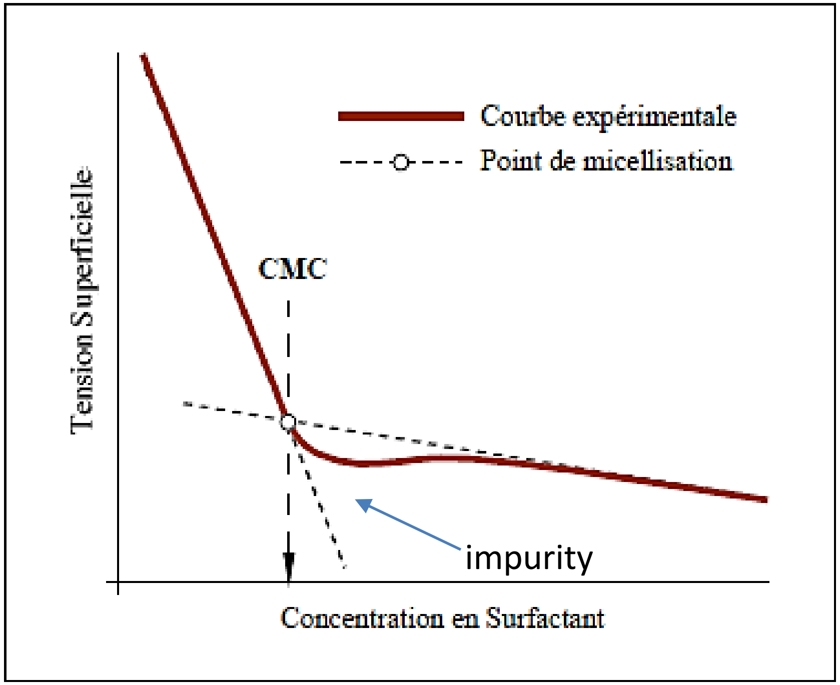
- The aggregation number (***NA****)* is the number of surfactant molecules (monomers) associated in a micelle (volume of micelle/volume of monomer)
- ***NA*** varies little from micelle to micelle.
- Each surfactant has a characteristic ***NA***, which is influenced by the
- *Temperature* and the *composition* of the micellar solution.

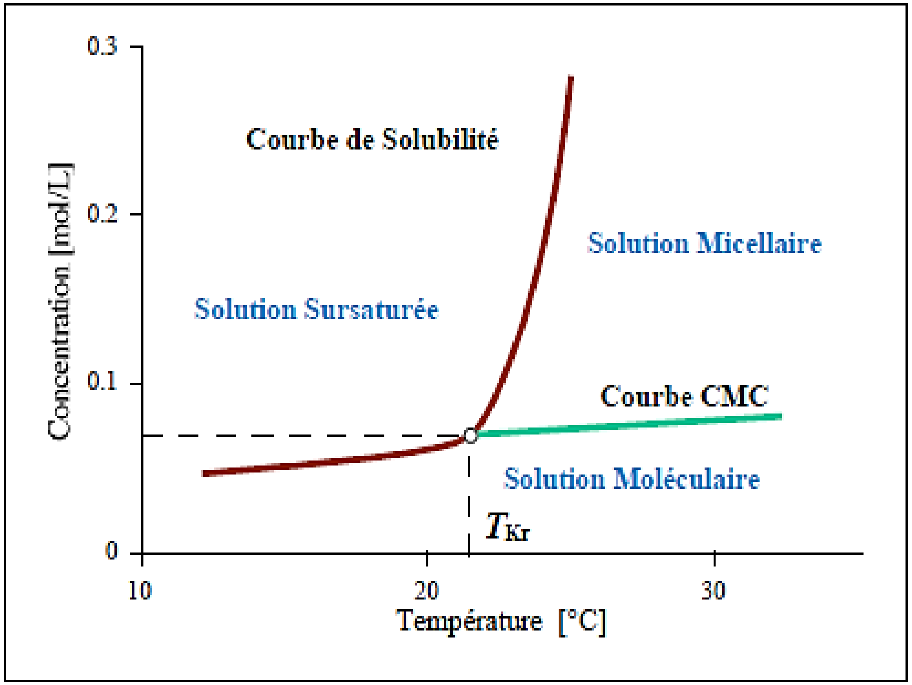


Amphiphilic Molecules - Solubility

Solubility diagram. *Krafft* Temperature

- The Concentration-Temperature diagram of a surfactant solution usually present *three* areas of stability:
  - molecular solution,
  - micellar solution,
  - solution supersaturated with surfactant (can crystalize hydrated surfactant crystals in time).
- The *triple point* of the diagram corresponds to the *Krafft* temperature of a surfactant.





Micellar Association - Association Reactions

General reaction

- The formation of a micelle can be treated as a succession of elementary chemical reactions such as:

$$\mathrm{S} + S_{n-1} \leftrightarrow S_n \qquad (4.1.1)$$

- Each reaction corresponds to an equilibrium constant (law of mass action):

$$K_n = \frac{[S_n]}{[S][S_{n-1}]} \qquad (4.1.2)$$

Close association model

- To account for the spontaneous formation of micelles with an almost constant degree of aggregation (n-micelles), we consider the overall reaction:

$$nS \leftrightarrow S_n \qquad (4.1.5)$$

Whose equilibrium constant is:

$$K_n = \frac{[S_n]}{[S]^n} \qquad (4.1.6)$$

- This is assuming that we go **directly from monomers to a micelle** without taking into account dimers, trimers, etc…i.e. **the close association model assumption**.

Micellar Association – Close Association Model

- For this model, the *total molar concentration* of surfactant {S} is given by:

  $\{S\} = n[S_n] + [S] = nK_n[S]^n + [S] = [S]\{1 + nK_n[S]^{n-1}\}$
  (4.1.7)

- We can consider three borderline cases.

  1. For the ***low free*** surfactant *concentrations* [S]:

     $$nK_n[S]^{n-1} << 1 \Rightarrow \log[S] \cong \log\{S\} \qquad (4.1.7a)$$

  2. For sufficiently *high* free surfactant concentration :

     $$nK_n[S]^{n-1} >> 1 \Rightarrow \log[S] \cong \frac{1}{n}\log\{S\} - \frac{1}{n}\log nK_n \qquad (4.1.7b)$$

  3. *half* surfactant is incorporated into the *n*-micelles (equi-partition) :

     $$[S]_0 = n[S_n]_0 = \frac{1}{2}\{S\}_0 \Rightarrow nK_n[S]_0^{n-1} = 1 \Rightarrow [S]_0 = (nK_n)^{\frac{-1}{n-1}} \qquad (4.1.7c)$$

where the concentration of free surfactant at equi-partition is noted $[S]_0$.

{S} = Total surfactant concentration
[S] = concentration monomers (free surfactant)
$[S]_0$ = equi-partition (50 % monomers – 50% in micelles)

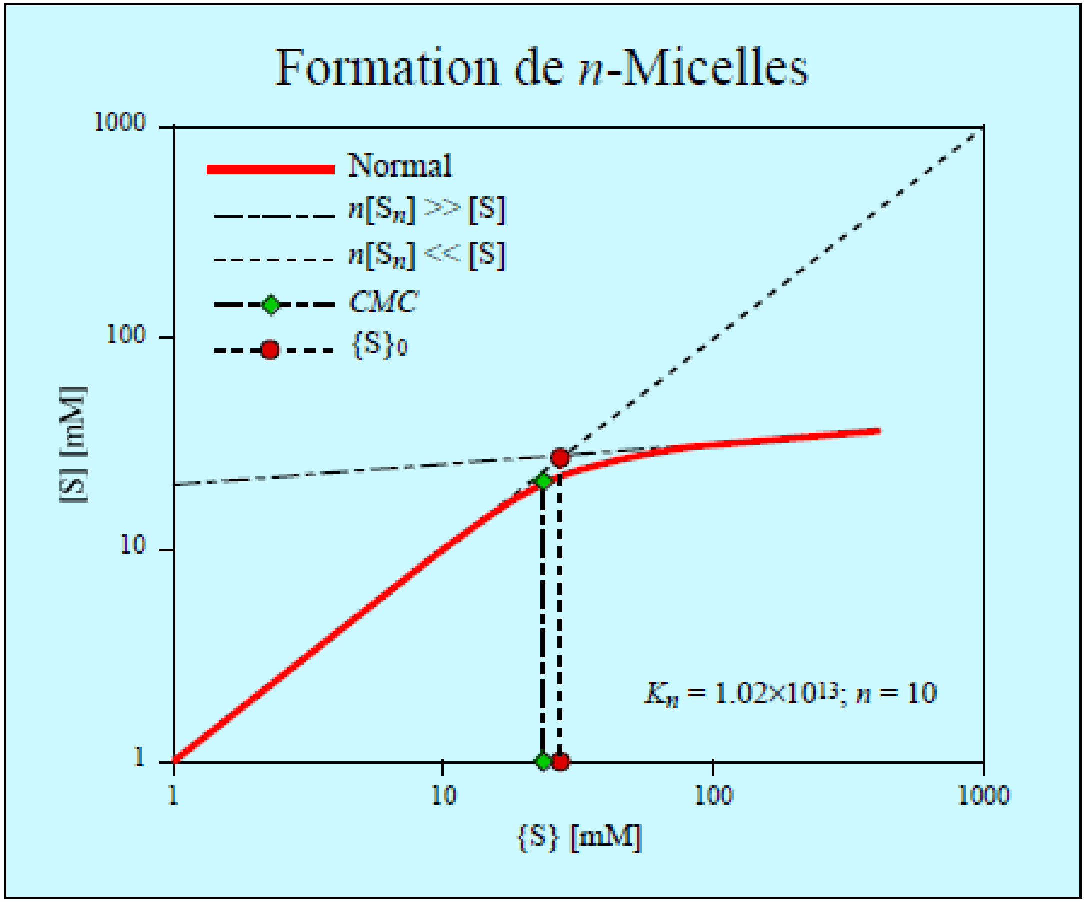
Micellar Association - Close association model

- For $\{S\} << [S]_0$ practically *all* the dissolved surfactant is in the *free* form – i.e. monomers

- When $\{S\} = \{S\}_0 = 2\,[S]_0$,
- 50% of the dissolved surfactant is in a *micellar* form .

- For $\{S\} >> [S]_0$ practically *all* the dissolved surfactant is in the *micellar* form :

$$\log[S] \cong \frac{1}{n}\log\{S\} - \frac{1}{n}\log nK_n$$



$\{S\}$ = Total surfactant concentration
$[S]$ = concentration monomers (free surfactant)
$[S]_0$ = equi-partition (50 % monomers – 50% in micelles)
$\{S\}_0 = 2\,[S]_0$ – N.B. log scale….

Micellar Association – Values of CMC

For a series of homologous surfactants:

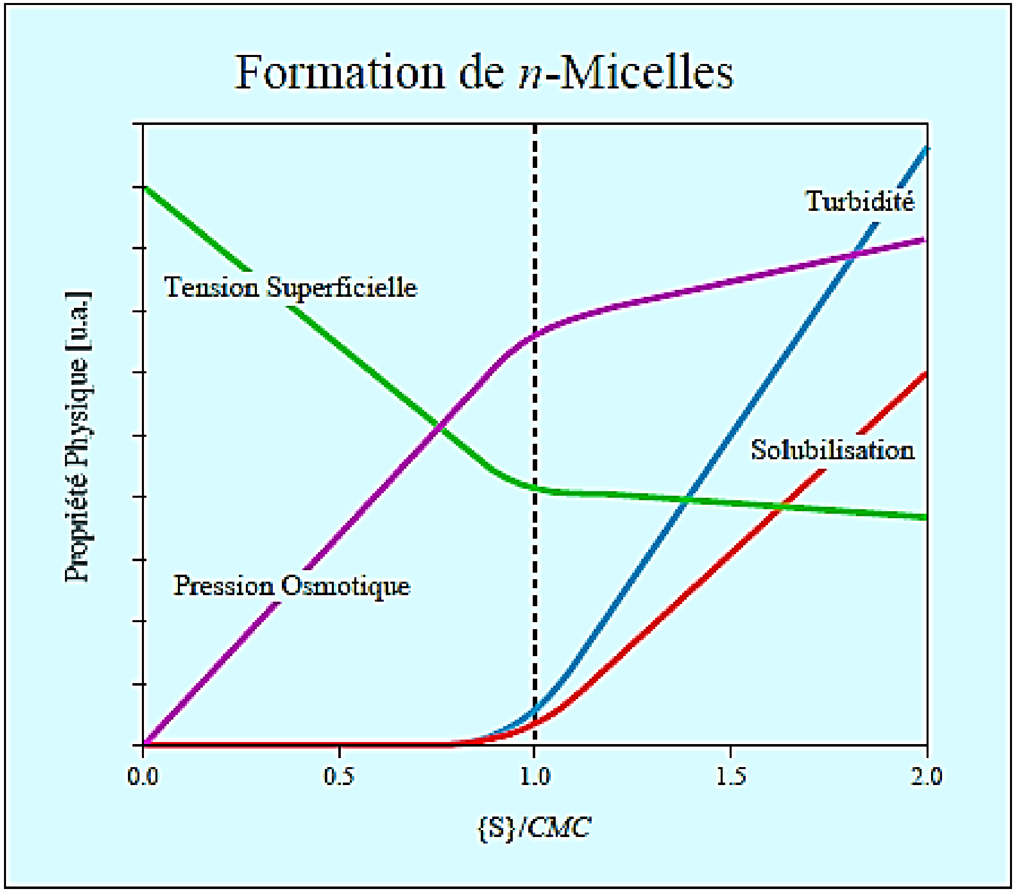
- The *CMC* decreases rapidly as the number of carbons in the alkyl chain increases.
- The aggregation number (NA, n) increases with the number of carbons in the alkyl chain.
- The aggregation number shows a certain dispersion around its average value *n*.

	Température	CMC	n	σ
Surfactant	[°C]	[M]	–	–
NaC_6SO_4	25	0.42	17	6
NaC_7SO_4	25	0.22	22	10
$NaC_{12}SO_4$	25	8.2×10^{-3}	64	13
$NaC_{14}SO_4$	40	2.1×10^{-3}	80	17

D'après EAG Aniansson et al., J. Phys. Chem. 80, 905 (1976).

Table 4.1. *CMC,* average aggregation number of *NA (n)* and standard deviation σ of the micelle size distribution for a series of sodium alkyl sulfates (determination from kinetic observations)

Micellar Association - Detection of micellization



With increasing concentration of surfactant, the evolution of **various** physical properties solutions suddenly change around the *CMC* :

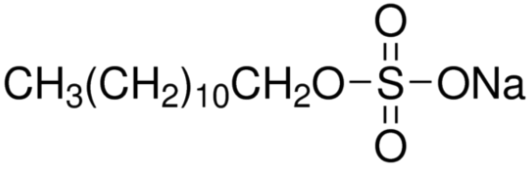
- decrease in surface tension;
- decrease in the increase of osmotic pressure ;
- sudden increase in turbidity;
- sudden increase in the capacity of the
- solution to dissolve Lyophobic substances (oils…).

For {S}> *CMC*, the evolution of physical properties provides information on the aggregation number *n (=NA)*.

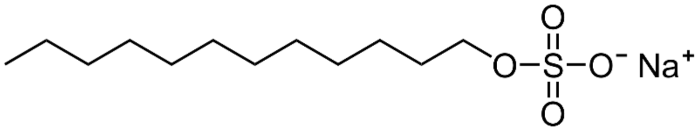
2

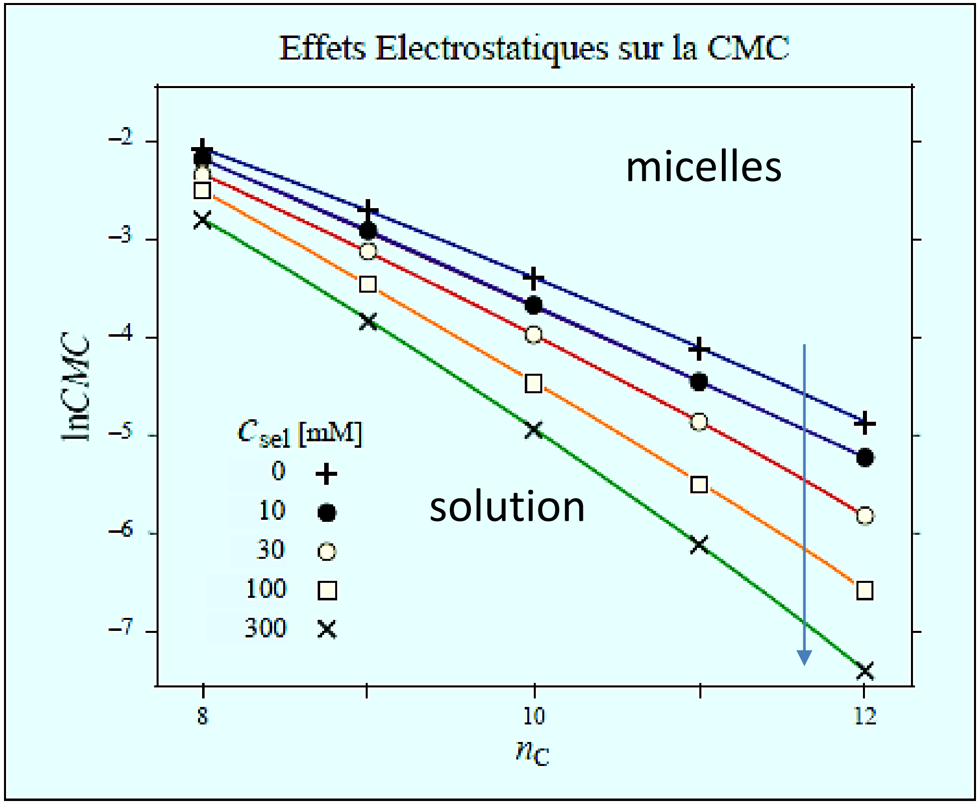
Micellar Association - Electrostatic Effects on *CMC*

- Effects of the length of the alkyl chain (n_c) and added salt (c_{salt}) at the C*MC* of SDS:
- SDS - Sodium Dodecyl Sulfate $NaC_{12}H_{25}SO_4$



$CH_3(CH_2)_{10}CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-ONa$





G. Gunnarsson B. Jonsson and H.Wennerstrom, *J. Phys. Chem.* **84**, 3114 (1980).

- the *CMC* decreases when n_c increases
- when c_{salt} increases, electrostatic repulsion between head groups decreases and lowers the *CMC;*
- the effect of c_{salt} is accentuated for surfactants with longer chains

Are you able to formulate a reasons for above effects, based on what we have seen in week 8?

Micellar Association - Electrostatic Effects on *CMC*

Non-ionic surfactants

- The absence of electric charge on the head groups **greatly reduces the *CMC*** of a nonionic surfactant relative to the ionic surfactant having an identical alkyl chain:

  $CMC(\mathrm{SDS}) = 8.3 \times 10^{-3}$ [M]

  $CMC(\mathrm{C_{12}E_8})^{*} = 7.1 \times 10^{-5}$ [M], with $\mathrm{E_8} = -(\mathrm{O}-\mathrm{C_2H_4})_8\mathrm{OH}$

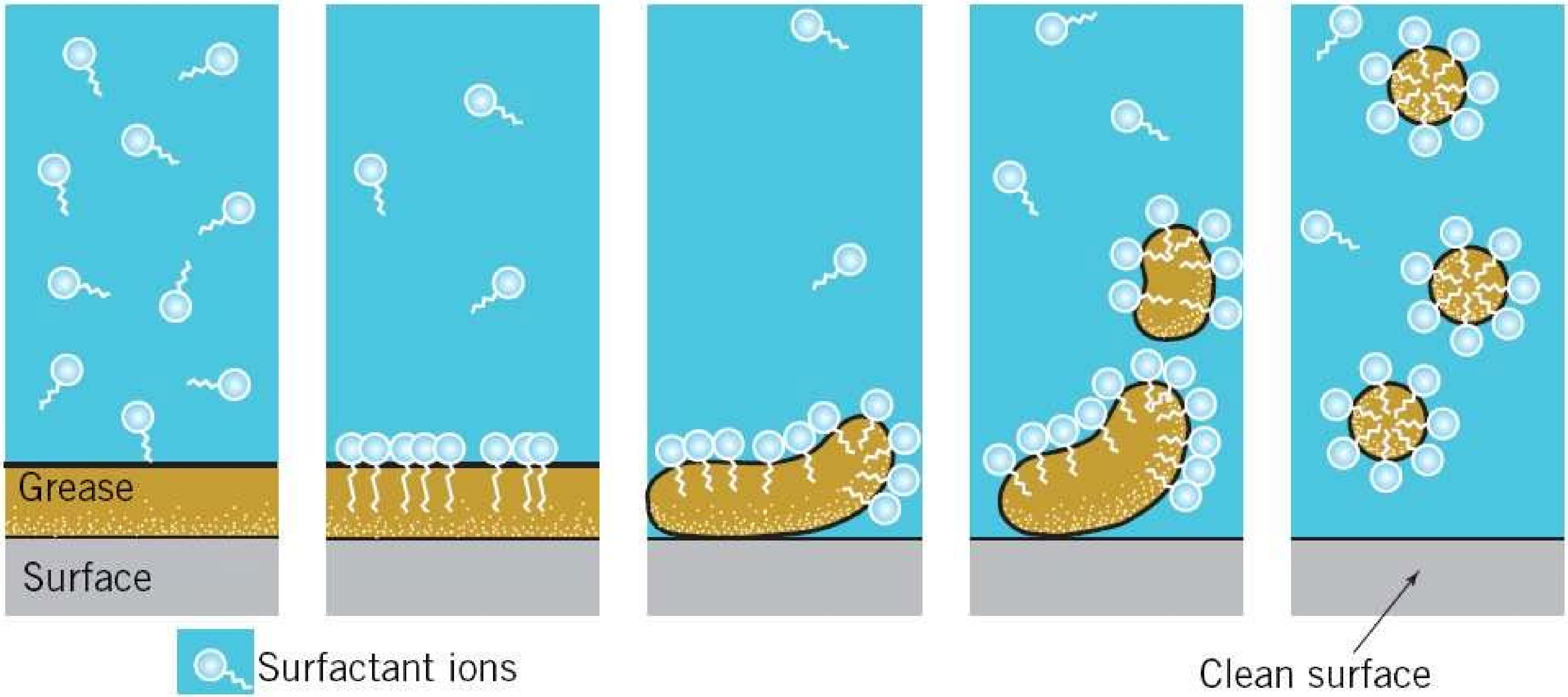
- Parallel dipole-dipole repulsions between head groups prevent a pure and simple phase separation of the surfactant.

Characteristics of non-ionic micellar solutions

- Micellar aggregates not very sensitive to c_{salt} ($c_{\mathrm{salt}} < 0.1$ M)
- Marked decrease in *CMC* at increasing temperature
- Increase in the aggregation number with increasing temperature
- Separation in two phases at high temperature: micelle rich phase and micelle poor phase.

*Dodecyl glycoside

Application -Detergents



(a)
Soap or detergent dissolves in water

(b)
Surfactant ions orientate themselves in grease and water

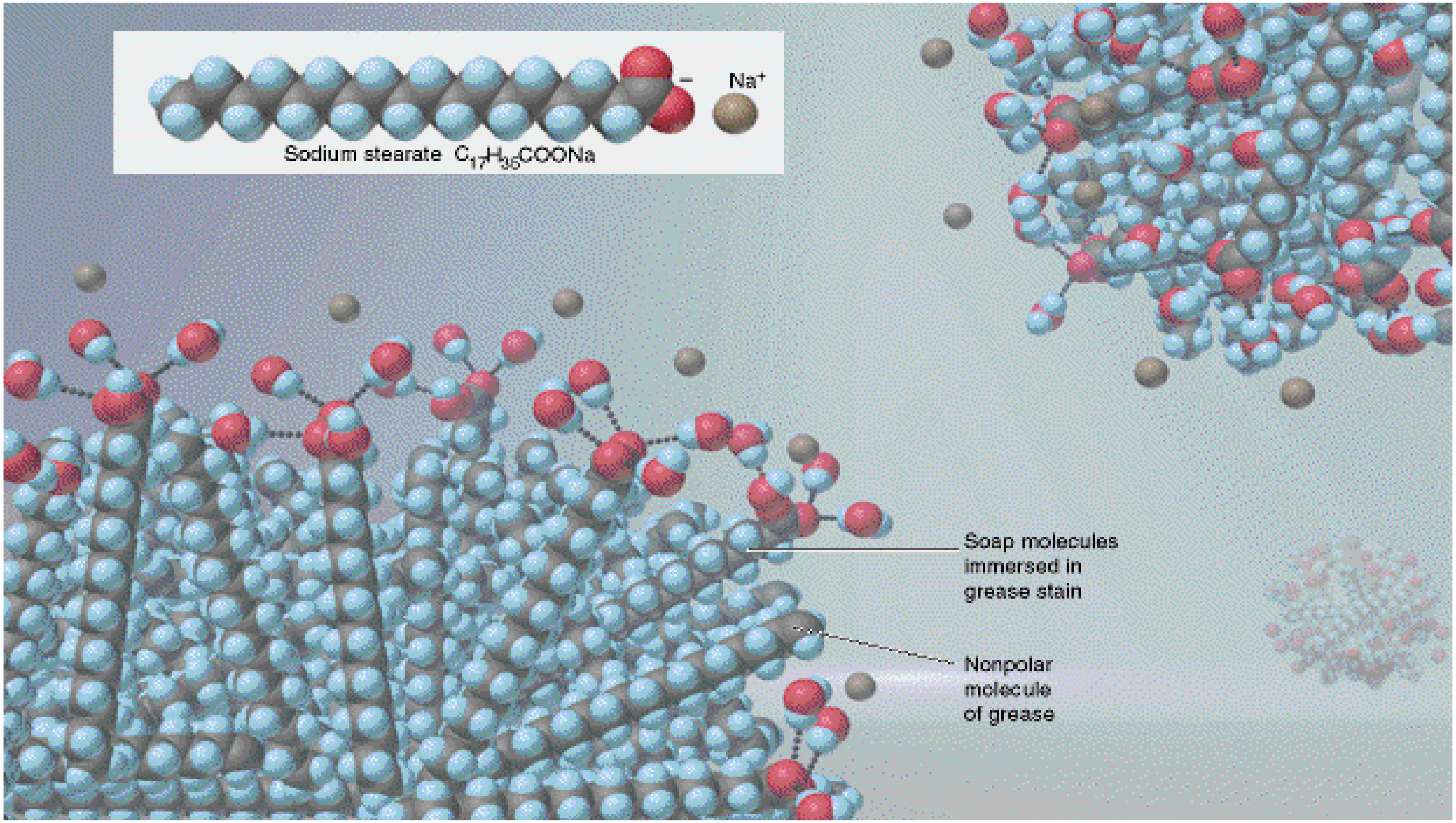
(c)
Agitation begins to separate grease from surface

(d)
Process continues

(e)
Cleaning complete

Application -Detergents

- **Detergents**



Application -Detergents

Detergents are mixtures of surfactants

Consider a mixture of two surfactants S_1, S_2, which can form an ideal binary mixture (surfactants of the same chemical family).

The chemical potential of S_i **in a micelle** is given by:

$$\mu_i(mic) = \mu_i^\theta(mic) + RT\ln x_i \qquad (4.4.1)$$

$\boldsymbol{x_i}$, mole fraction of S_i in a **mixed micelle**: $x_1 + x_2 = 1$

The chemical potential of S_i **in the solution** :

$$\mu_i(sol) = \mu_i^\theta(sol) + RT\ln c_i \qquad (4.4.2)$$

If $\boldsymbol{\alpha_i}$ is the mole fraction of S_i in **the initial binary mixture** of S_1, S_2 ($\alpha_1 + \alpha_2 = 1$):

$$c_i = \alpha_i c_{Tot} \qquad (4.4.3)$$

at the critical micellar concentration CMC_i of each of the surfactants:

$$\mu_i(mic) = \mu_i^\theta(sol) + RT\ln CMC_i \qquad (4.4.4)$$

Application - Detergents

Ideal mixture of surfactants S_1, S_2

At CMC_{tot}, the CMC of the mixture (S_1, S_2), is reached :

$$\mu_i(mic) = \mu_i(sol); i = 1,2 \qquad (4.4.5)$$

The combination of Eq. (4.4.1) to (4.4.4) then allows us to conclude that:

$$\frac{1}{CMC_{Tot}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \qquad (4.4.6)$$

The respective mole fractions of S_1 and S_2 in the micelles are then:

$$x_i = \frac{\alpha_i CMC_{Tot}}{CMC_i}; i = 1,2 \qquad (4.4.7)$$

NB : these conclusions are only valid for the CMC_{tot}.

- At higher concentrations, the balance between solution and micelles, which depends on the size and aggregation number, micelles are in equilibrium with a solution of a given composition.
- **Example :** $\alpha_1 = \alpha_2 = 50.0\%$ initial solution composition ;
- $CMC_1 = 8.20$ [mM]; $CMC_2 = 2.05$ [mM]
- This gives $CMC_{tot} = 3.29$ [mM], $x_1 = 20.0\%$ and $x_2 = 80.0\%$.
- The composition of the micelle is different to the initial solution and favours a lower CMC

Application -Detergents

Mixtures of any surfactants

- As with any molecular mixture, the *interaction energy* between the constituents of the mixture S_1, S_2 has to be taken into account:

Interaction parameter w <2kT :

Surfactants are miscible in *all proportions* : there is only one type of micelle.

Interaction parameter $w > $ 2kT :

Under certain conditions, surfactants can form *two populations* micelles,

some rich in S_1, the others rich in S_2.

In addition, it should be noted that:

- The addition of a non-ionic surfactant to an ionic surfactant reduces the electrostatic charge of co-micelles, and therefore lowers the *CMC*.
- The mixture of ionic surfactants of opposite charges makes it possible to form co-micelles at very low electrostatic charge.
- The effect of adding a little ionic surfactant to a non-ionic surfactant increases electrostatic repulsion at long distance between micelles.