Introduction to the colloid chemistry and surface phenomena

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Examples of colloidal systems
and surface phenomena from daily life

How detergents really clean?

And why this “milky” colour that milk has?

Why do mosquitos and other small insects can walk on water?

Why does Ouzo’s colour change from transparent to cloudy when we add water?

Why the leaves of lotus possess self-cleaning property?

Why do we so often use eggs for making sauces?

More examples of colloids

Historical note: The term ‘colloid’ is derived from the Greek word ‘kolla’ for glue. It was originally used for gelatinous polymer colloids, which were identified by Thomas Graham in 1860 in experiments on osmosis and diffusion.

Colloid science is both a multi- and interdisciplinary topic

Physical chemistry

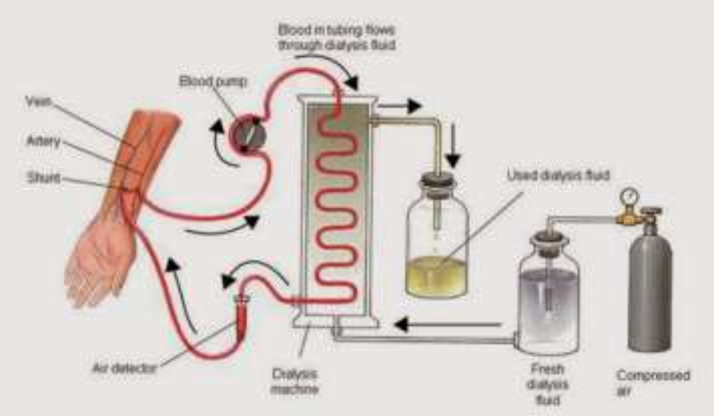
Physics

Biology

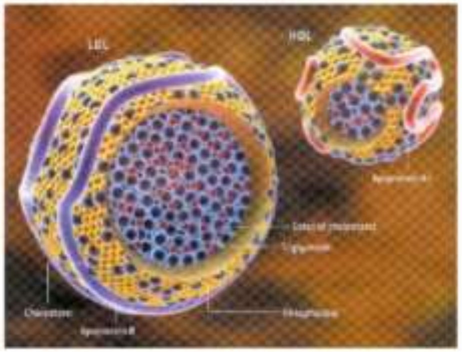
Medicine

Materials

Microelectronics

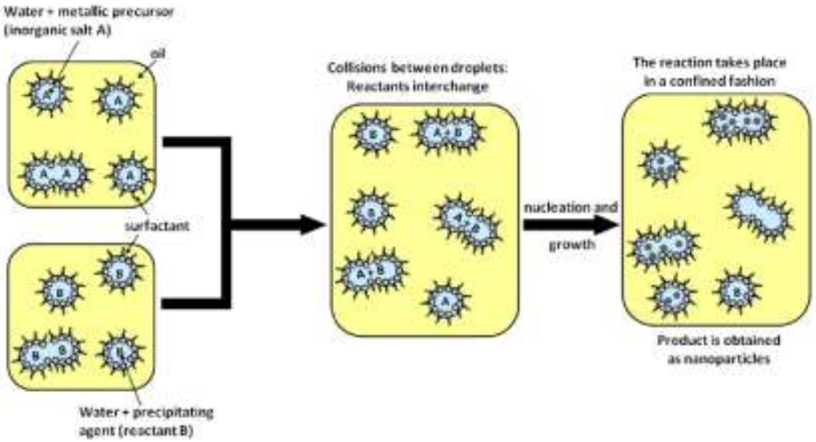


Dialysis



HDL, High-Density Lipoprotein, 8–11 nm sized biomolecule aggregates containing cholesterol, phospholipids, apolipoproteins A etc. ("good cholesterol")

LDL, Low-Density Lipoprotein, 18–25 nm sized similar aggregates ("bad cholesterol")



Microemulsion synthesis

Truly valuable to chemists, chemical engineers, biologists, material and food scientists and many more.

Definition of colloidal systems

Finely-divided dispersion of one phase in another.

It concerns, in the main, systems containing large molecules and/or small particles.

The adjective 'microheterogeneous' provides an appropriate description of most colloidal systems.

There is, however, no sharp distinction between colloidal and non-colloidal systems.

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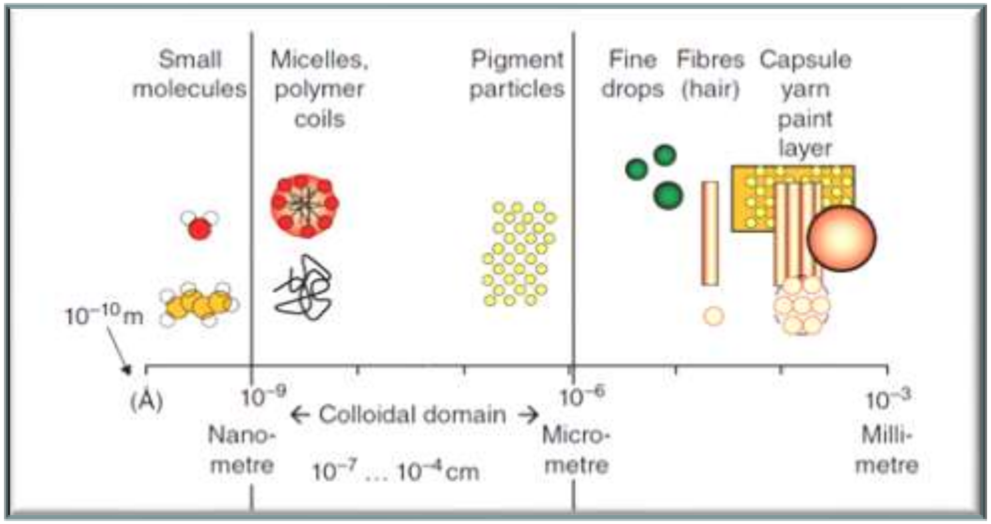
What are the colloids and interfaces? Why do we study them together?

Colloidal dispersions are systems of particles or droplets with the "right dimensions" (the dispersed phase), which are dispersed in a medium (gas, liquid or solid).

But which are the "right dimensions"?



The link between colloids and surfaces follows naturally from the fact that particulate matter has a high surface area to mass ratio.

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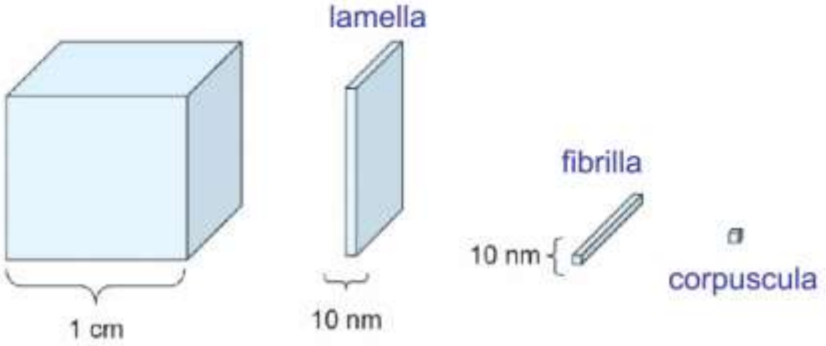
Surface matters

The characteristic properties of colloidal systems are due to the size of the particles or droplets (i.e. the dispersed phase), and not to any special nature of the particles

Their high interfacial area is the reason why colloidal systems have special properties and also why we study colloids and interfaces together.



N	1	10^6	10^{12}	10^{18}
A_1 (cm²)	6	2	4×10^{-6}	6×10^{-12}
A_{tot} (cm²)	6	2×10^6	4×10^6	6×10^6

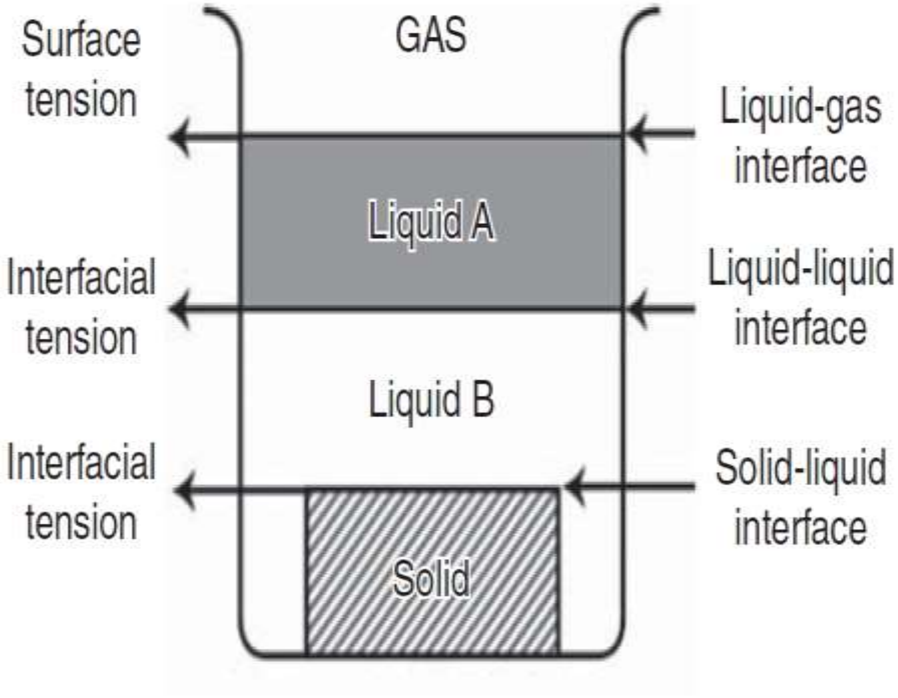
Another example

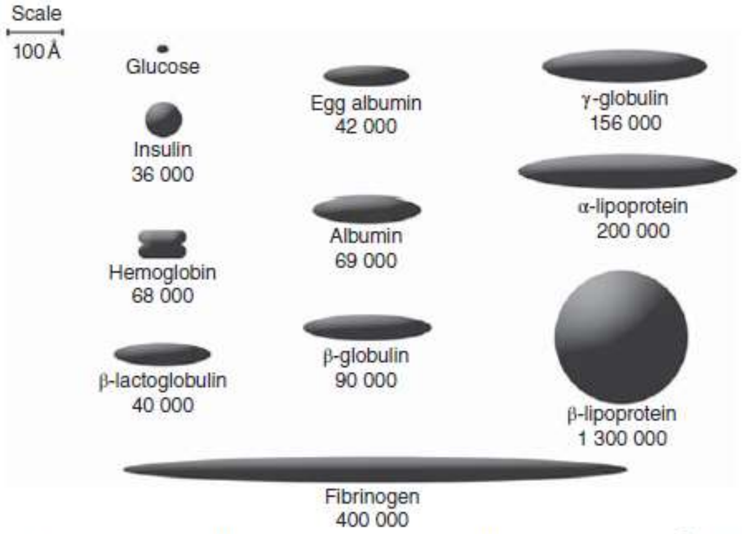
1 litre of a latex paint suspension containing 50% solids with a particle size of 0.2 μm has a total particle surface area of 15000 m^2*.*

However, to form such huge interfaces, e.g. by dispersing water in the form of droplets in an oil, we need "to do a lot of work".

Colloids and interfaces

An interface has a thickness of afew ångstrøm





Different shapes of colloid particles with molecular weights provided in g mol^{-1}. Pr J. L. Onclev

Why are colloids important?

It is a highly interdisciplinary subject, of interest to diverse fields of science and engineering.

Just to mention a few: pharmaceuticals, food, cosmetics, detergents, medicine and biology, up to materials and microelectronics.

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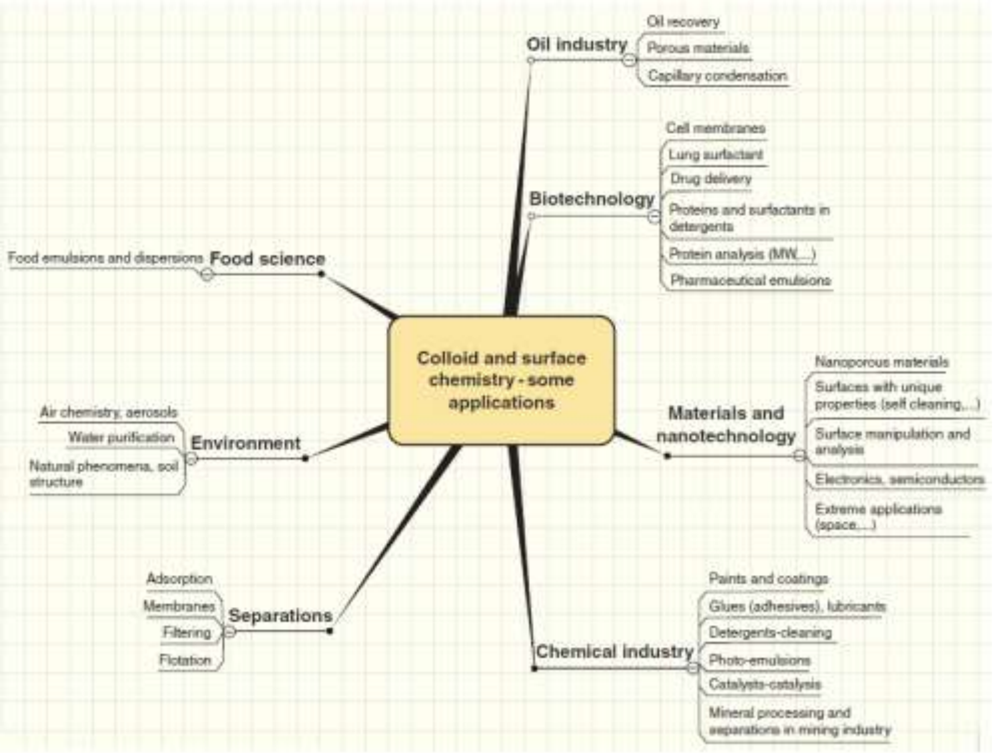
Some applications



Colloid and surface chemistry - some applications

- **Oil industry**
  - Oil recovery
  - Porous materials
  - Capillary condensation
- **Biotechnology**
  - Cell membranes
  - Lung surfactant
  - Drug delivery
  - Proteins and surfactants in detergents
  - Protein analysis (MW,...)
  - Pharmaceutical emulsions
- **Materials and nanotechnology**
  - Nanoporous materials
  - Surfaces with unique properties (self cleaning,...)
  - Surface manipulation and analysis
  - Electronics, semiconductors
  - Extreme applications (space,...)
- **Chemical industry**
  - Paints and coatings
  - Glues (adhesives), lubricants
  - Detergents-cleaning
  - Photo-emulsions
  - Catalysts-catalysis
  - Mineral processing and separations in mining industry
- **Separations**
  - Adsorption
  - Membranes
  - Filtering
  - Flotation
- **Environment**
  - Air chemistry, aerosols
  - Water purification
  - Natural phenomena, soil structure
- **Food science**
  - Food emulsions and dispersions

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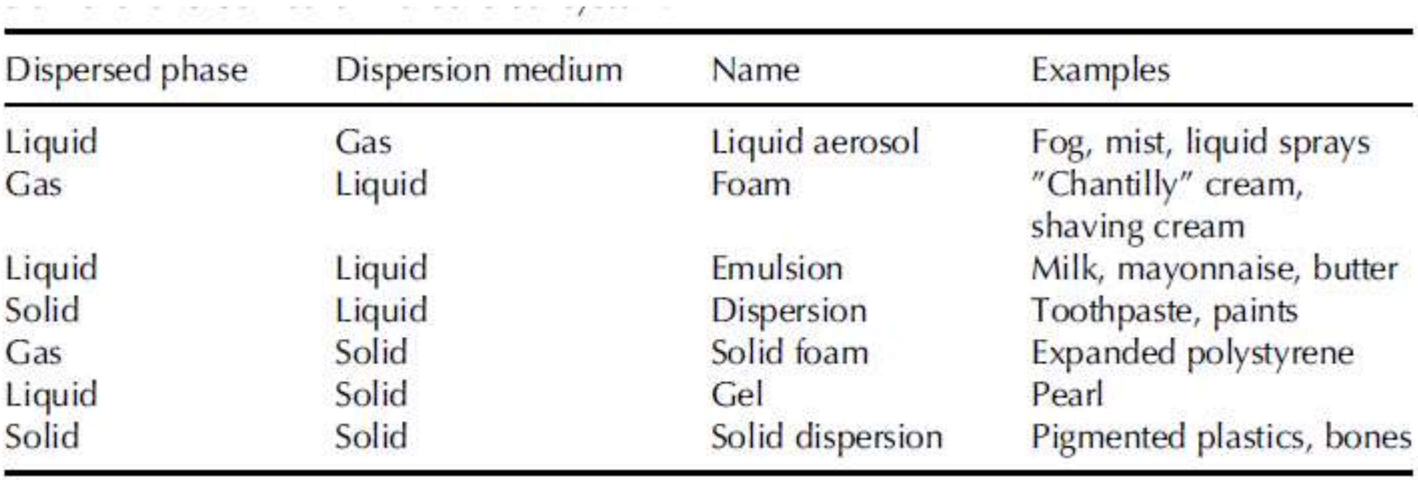
Three ways of classifying the colloids

Colloids (or colloidal dispersions) can be classified according to the state of the dispersed phase and the dispersion medium (gas, liquid, solid).

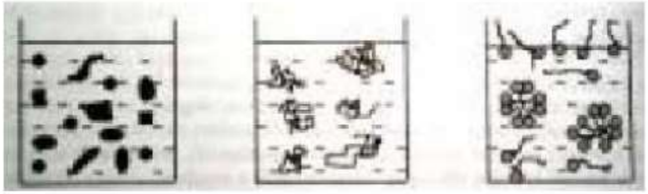


Dispersed phase	Dispersion medium	Name	Examples
Liquid	Gas	Liquid aerosol	Fog, mist, liquid sprays
Gas	Liquid	Foam	"Chantilly" cream, shaving cream
Liquid	Liquid	Emulsion	Milk, mayonnaise, butter
Solid	Liquid	Dispersion	Toothpaste, paints
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Gel	Pearl
Solid	Solid	Solid dispersion	Pigmented plastics, bones

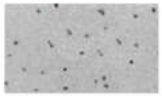
Classification

colloids

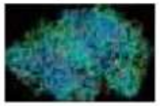
- incoherent systems
  - colloidal dispersions
  - macromolecular solutions
  - association colloids
- coherent systems (gels)
  - porodin
  - reticular
  - spongoid



liophobic



liophilic



liophilic

corpuscular fibrillar lamellar

Lyophobic and Lyophilic

Lyophobic (i.e. solvent hating) colloids are those in which the dispersoid (dispersed object) constitutes a distinct phase.

Lyophobic colloids are thermodynamically unstable.

Lyophilic colloids refer to single-phase solutions of macromolecules or polymers.

These terms describe the tendency of a particle (in general a chemical group or surface) to become wetted/solvated by the liquid.

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How to prepare colloid systems?

Basically, the formation of colloidal material involves either degradation of bulk matter or aggregation of small molecules or ions.

Dispersion of bulk material by simple grinding in a colloid mill or by ultrasonics

Aggregation methods involve the formation of a molecularly dispersed supersaturated solution from which the material in question precipitates in a suitably divided form.

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Key properties of colloids

They have very interesting kinetic, rheological and optical properties.

The van der Waals attractive forces in colloids are much stronger than those between molecules and lead to aggregation (instability), but there are (fortunately) also repulsive electrical forces, when the particles are charged, which "help stability".

There are other types of repulsive forces, e.g. steric, solvation.

Almost all lyophobic colloids are in reality metastable systems.

When we use the term "stable" colloids, we imply a kinetically stable colloid at some arbitrary length of time (which can be, forexample, two days or two years).

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Author, Editor and Referee References

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References and Supplemental Material

The NETCHEM platform was established at the University of Nis in 2016-2019 through the Erasmus Programme.

Please contact a NETCHEM representatives at your institution or visit our website for an expanded contact list.

The work included had been led by the NETCHEM staff at your institution.

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Colloid Stability –The Major Players (van der Waals and Electrical Forces)

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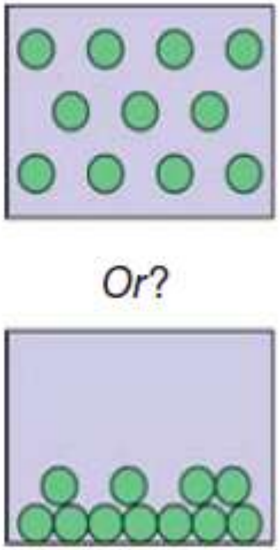
Key forces and potential energy plots

Colloidal dispersions have a high interfacial area and are therefore unstable; they have to be stabilized.

The most important forces are:

- the van der Waals (vdW) forces, which are usually attractive and are the cause of instability
- the, usually, repulsive forces due to electrical charges on the particles.



Colloid stability

Determined by forces between particles:

🟩 Elastic	*Repulsive*
🟩 van der Waals	*Attractive*
🟩 Electrical (ions)	*Repulsive*
🟩 Steric (polymers)	*Repulsive*

↑ Usually!

Colloid stability and mechanical stability

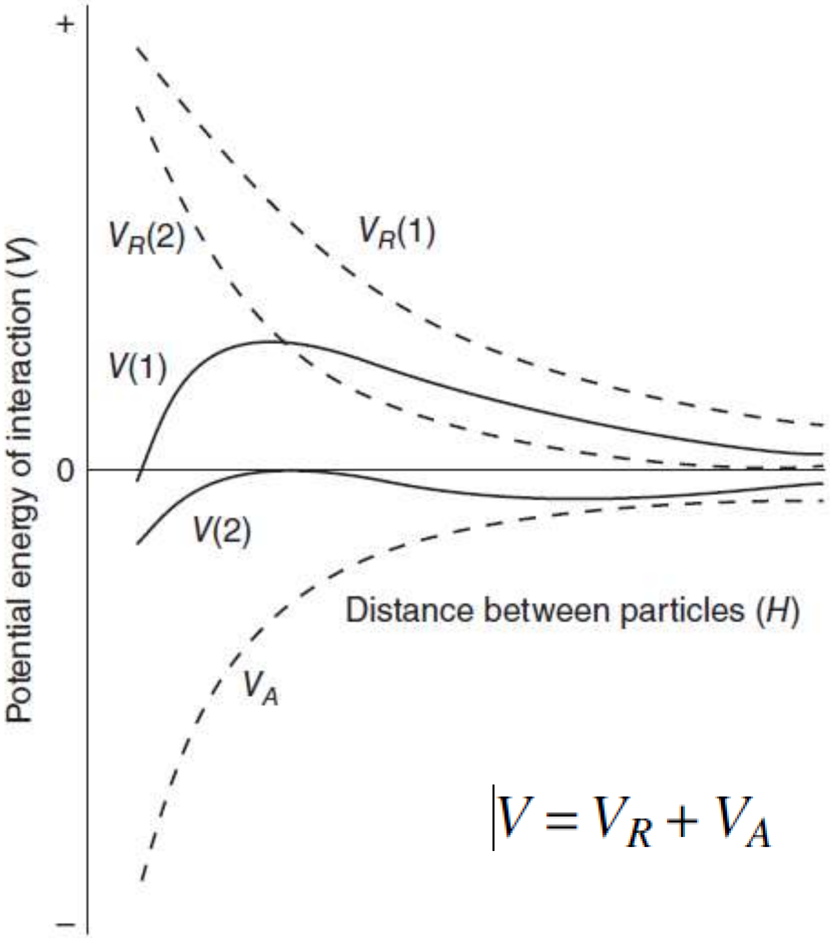
The colloid stability of a dispersion refers to small particles that do not aggregate (in the practical lifetime of the dispersion).

The mechanical stability refers to dispersed particles that do not sediment or cream.

Interactions

The potential energy–distance plot (V–H curves) represents graphically the behaviour of a colloidal system.

The stability of colloidal dispersions is often described quantitatively via the DLVO (Derjaguin–Landau–Verwey–Overbeek)



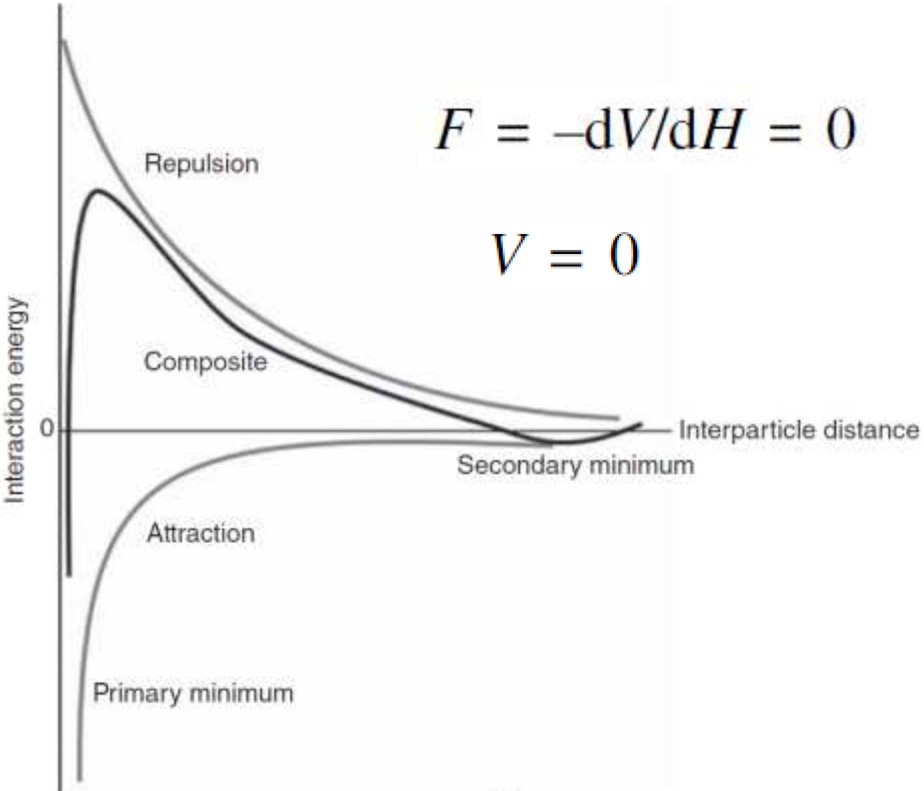
$$V = V_R + V_A$$

Critical coagulation concentration (CCC)

In DLVO the total potential energy is expressed as simply the sum of the repulsive and the attractive energy.

Equation for V in the slide is for equal-sized spherical particles of equal and small surface potentials (less than 25 mV for 1 : 1 electrolytes) and small electric double layer overlap.

For very small particles (radius less than about 10 nm) the secondary minimum is not deep enough to get flocculation.



$$F = -\mathrm{d}V/\mathrm{d}H = 0$$

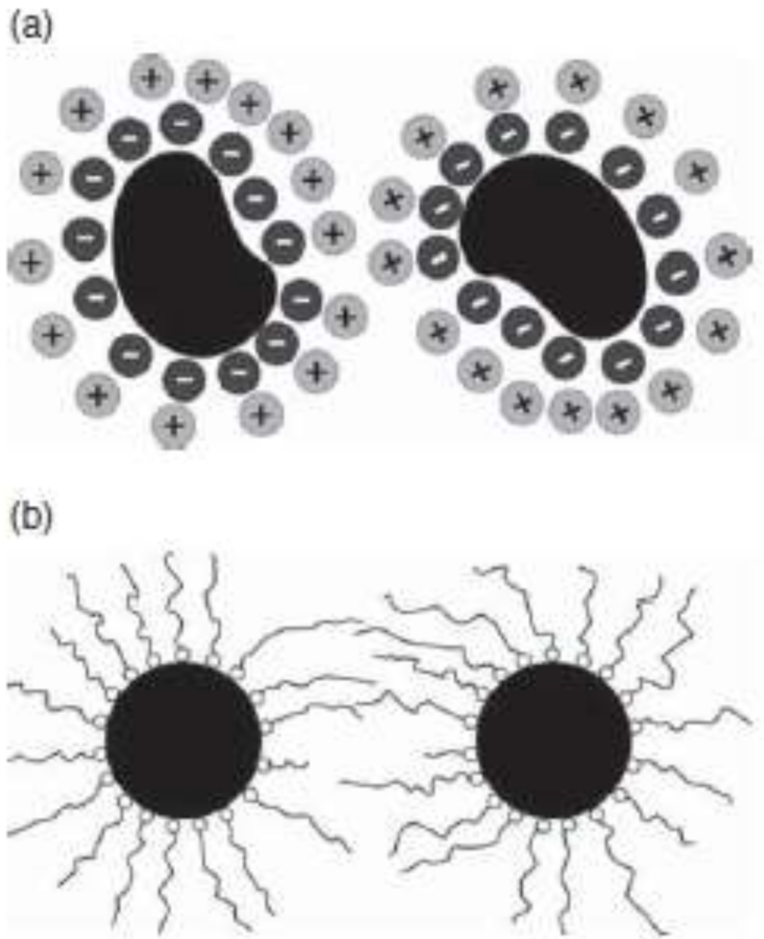
$$V = 0$$

$$V = V_R + V_A = 2\pi R\varepsilon\varepsilon_0\psi_0^2\exp(-\kappa H) - \frac{AR}{12H}$$

vdW and electrostatic forces

- are long-range (vdW forces dominate at high and small distances, electrostatic forces may dominateat intermediate distances);
- depend on the characteristics of the particles and the medium;
- depend greatly on the shape of the particles/surfaces (e.g. sphere, plates, cylinders), their size and proximity.

Electrical and steric stabilization



Schematic representation of the electrical double-layer forces (a) and of the steric (or entropic) stabilization (b).

vdW forces

Colloid stability assumes a balance between the van der Waals (vdW) forces (typically attractive) and the (typically repulsive) electric (double-layer) forces.

Attractive vdW forces between particles and surfaces are much more long-range (they can be of importance at distances as high as 100 nm) than the vdW forces between molecules

Gecko on the glass (vdW forces)

van der Waals force between equal-sized spherical colloidal particles when $H << R$

$$V_A = -\frac{AR}{12H}$$

The vdW forces depend on the size and shape (geometry) of particles/surfaces and their proximity but above all they depend on the nature (chemistry) of the materials and the medium via the so-called Hamaker constant, A.

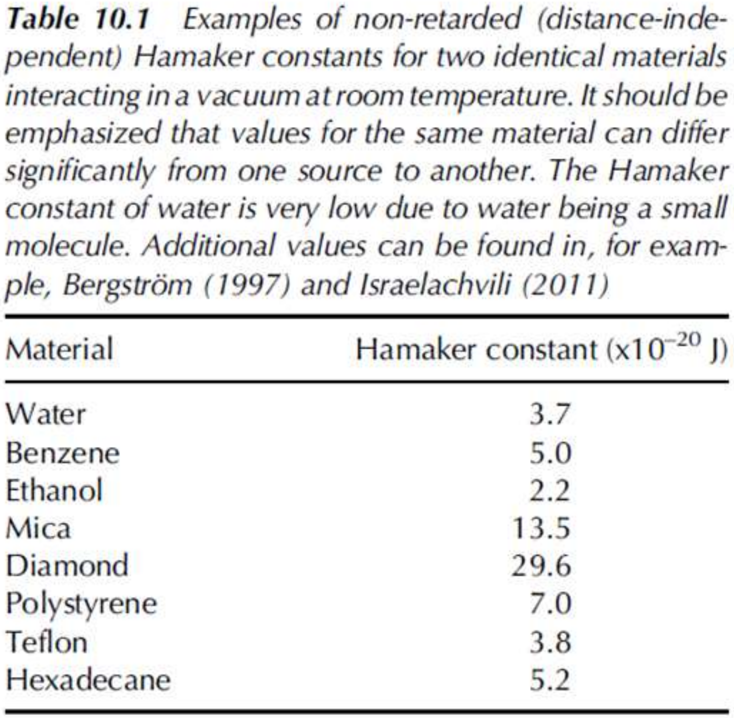


Table 10.1 *Examples of non-retarded (distance-independent) Hamaker constants for two identical materials interacting in a vacuum at room temperature. It should be emphasized that values for the same material can differ significantly from one source to another. The Hamaker constant of water is very low due to water being a small molecule. Additional values can be found in, for example, Bergström (1997) and Israelachvili (2011)*

Material	Hamaker constant ($\times 10^{-20}$ J)
Water	3.7
Benzene	5.0
Ethanol	2.2
Mica	13.5
Diamond	29.6
Polystyrene	7.0
Teflon	3.8
Hexadecane	5.2

Eeffective value of the Hamaker constant in a medium other than vacuum or air

when we have the same type of particles in a medium

$$A_{eff} = A_{121} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2$$

the effective Hamaker constant in the case of two different types of particles (1 and 3) in a medium 2 is

$$A_{eff} = A_{123} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{22}}\right)$$

The effective Hamaker constant can be negative, which implies repulsive van derWaals forces.

Some examples of effective Hamaker constants

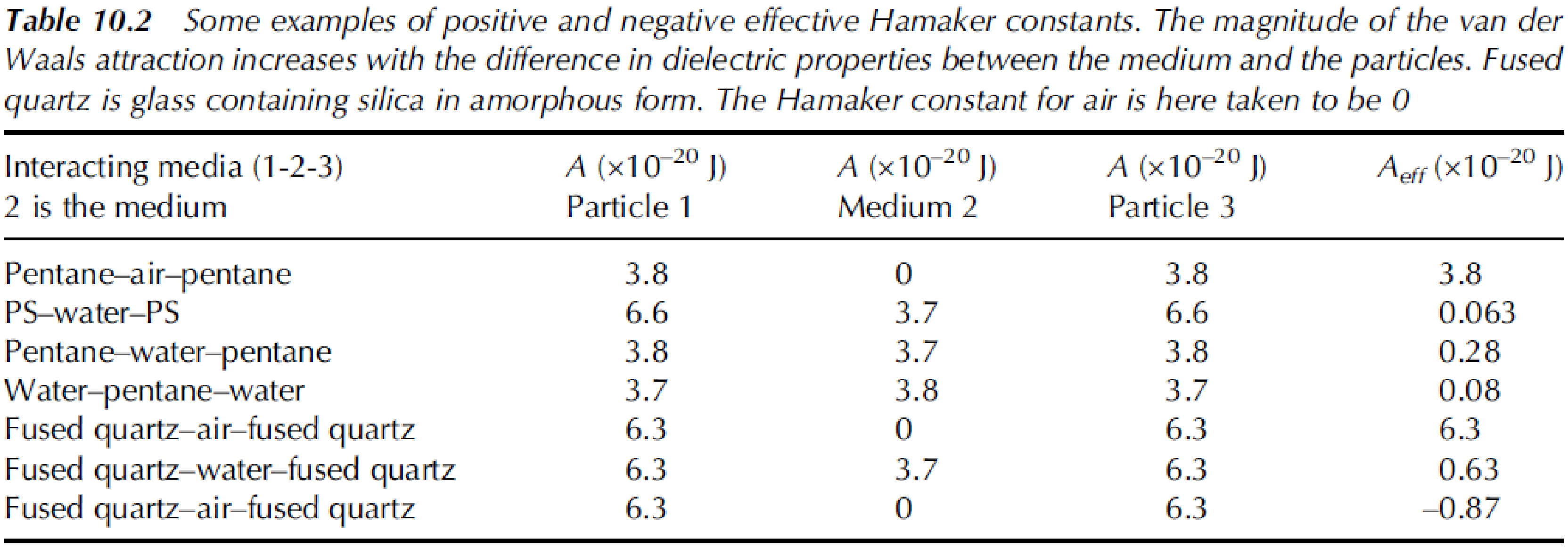


Table 10.2 *Some examples of positive and negative effective Hamaker constants. The magnitude of the van der Waals attraction increases with the difference in dielectric properties between the medium and the particles. Fused quartz is glass containing silica in amorphous form. The Hamaker constant for air is here taken to be 0*

Interacting media (1-2-3) 2 is the medium	A ($\times 10^{-20}$ J) Particle 1	A ($\times 10^{-20}$ J) Medium 2	A ($\times 10^{-20}$ J) Particle 3	A_{eff} ($\times 10^{-20}$ J)
Pentane–air–pentane	3.8	0	3.8	3.8
PS–water–PS	6.6	3.7	6.6	0.063
Pentane–water–pentane	3.8	3.7	3.8	0.28
Water–pentane–water	3.7	3.8	3.7	0.08
Fused quartz–air–fused quartz	6.3	0	6.3	6.3
Fused quartz–water–fused quartz	6.3	3.7	6.3	0.63
Fused quartz–air–fused quartz	6.3	0	6.3	–0.87

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vdW forces for different geometries - examples

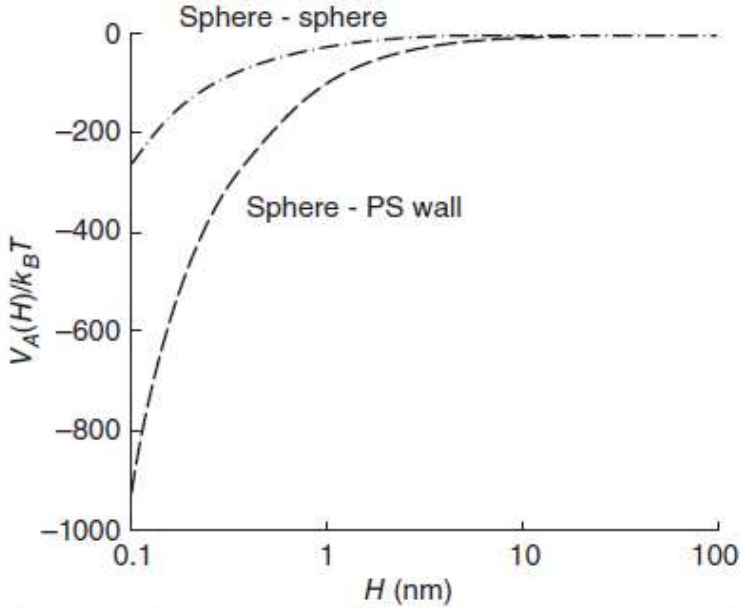


Figure 10.5 *Attractive interaction between tetradecane (C_{14}) spheres and between spheres and the polystyrene (PS) wall they are contained in. Adapted from Goodwin (2009), with permission from John Wiley & Sons, Ltd*

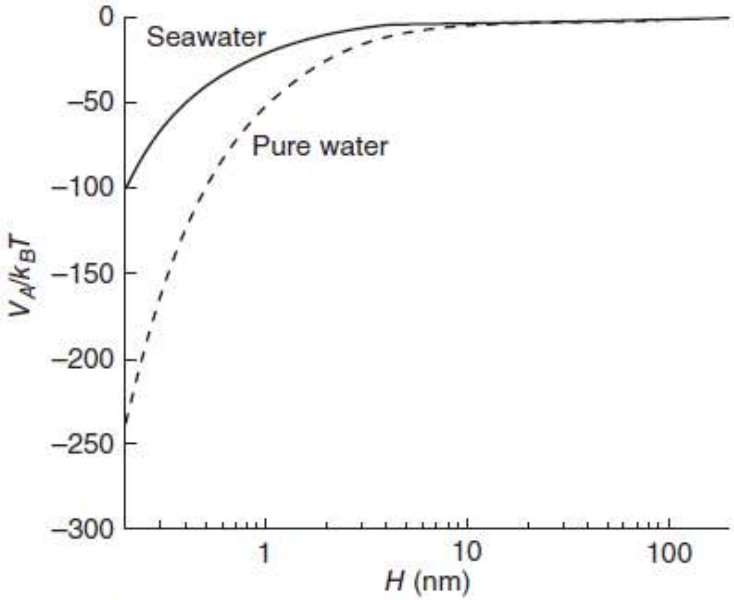


Figure 10.6 *Oil (C_{14}) droplets in water and seawater. In seawater, the oil droplets are less sticky. The difference is due to the Hamaker constants in the two liquids. Adapted from Goodwin (2009), with permission from John Wiley & Sons, Ltd*

Electrostatic forces: the electric double layer and the origin of surface charge

The interfaces may have a positive or negative charge, but the latter (negative) is the most common.

Charge depends on pH, nature of surface groups and salt concentration.

Most surfaces are negatively charged, since the smaller cations are typically more hydrated than anions.

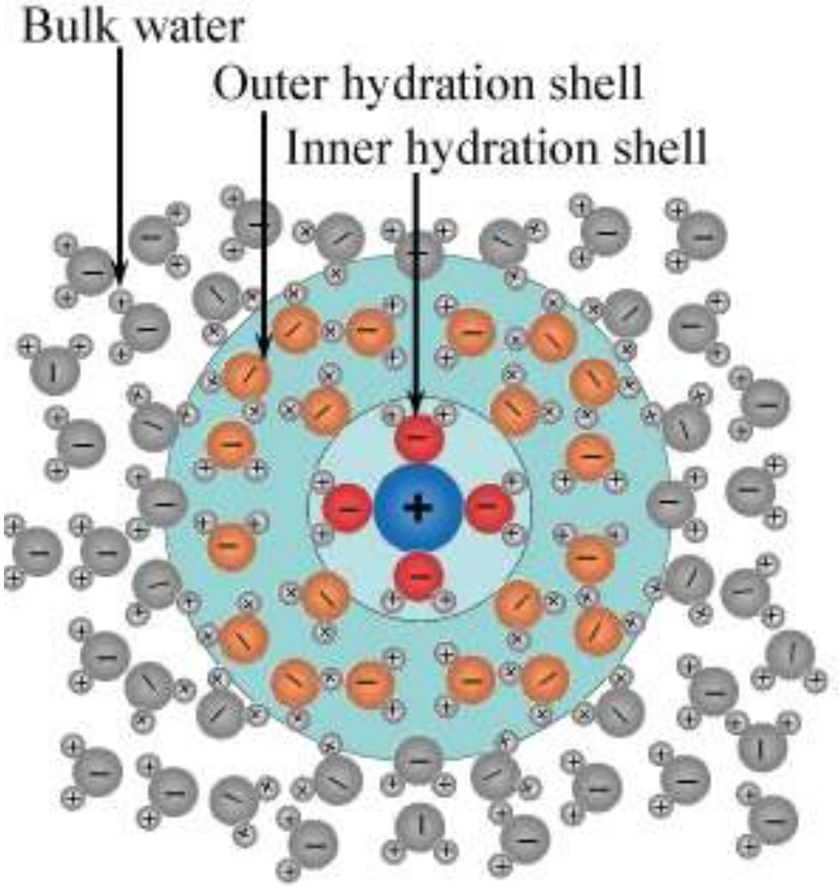
Thus the cations remain in aqueous solution, while the anions adsorb on the surface.

Hydratation

Hydration of counter-ions is good because it restricts the ability to approach the particle surface and enter the Stern layer.

Consequently, less destabilization by hydrated ions is obtained.

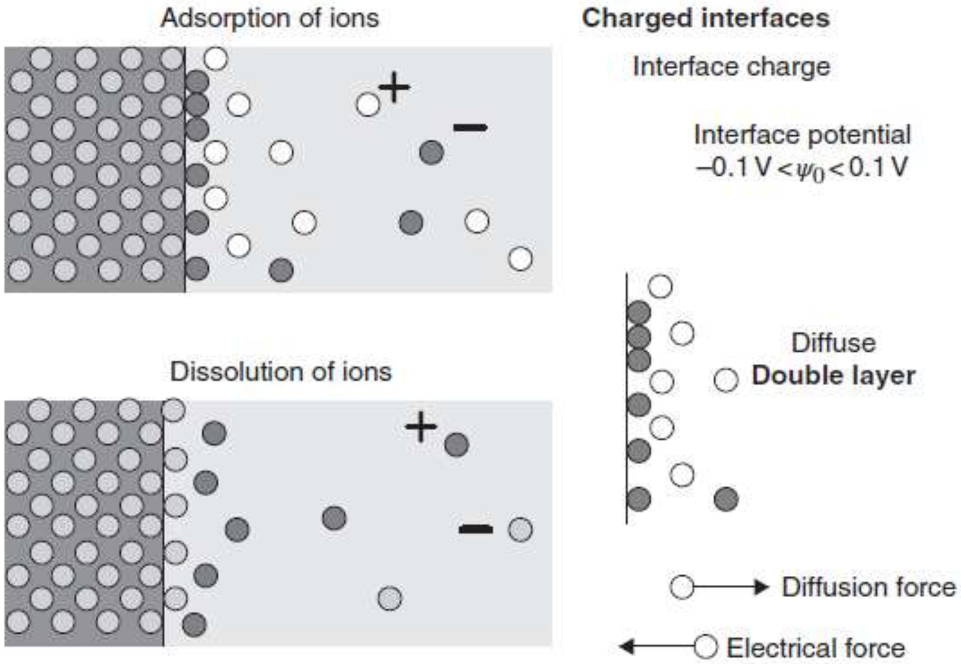
Ionic valency also plays an important role in itself (the Schulze-Hardy rule).



Charged interfaces

In the diffuse double-layer model, the ionic atmosphere consists of two regions: a so-called Stern (or near-Ste

after that.

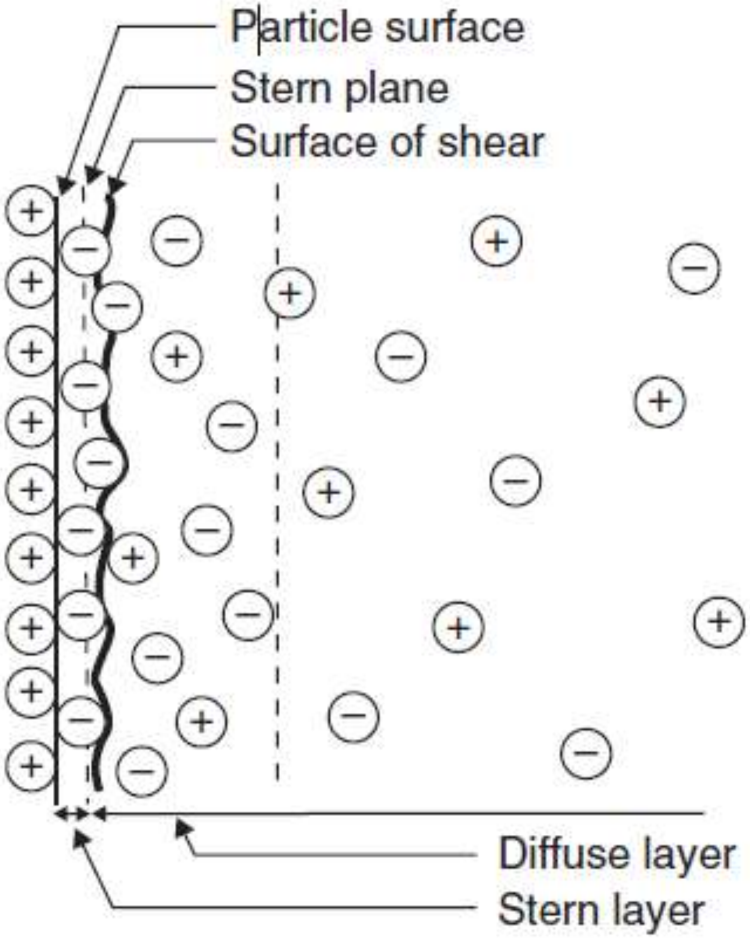


The surface of shear

The exact location of the surface of shear, of great importance for the measurement of the“zeta potential” .

It is considered to be qui close to the Stern plane.

The net charge of the Stern layer, diffuse layer, and the surface is zero because of electroneutrality



Why are the surfaces or particles charged?

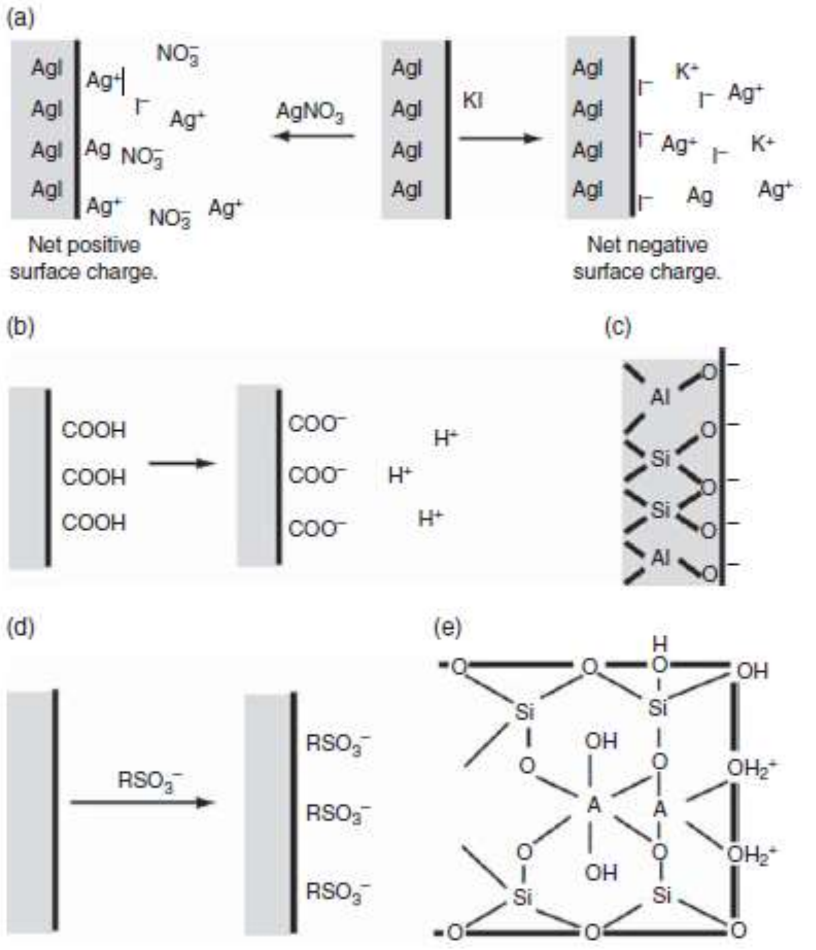
Differential ion solubility;

direct ionization of surface groups;

isomorphous substitution;

specific ion adsorption; and

anisotropic crystals



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Sources of surface charge in colloids

Adsorption of surface ions, e.g. ionic crystals, AgCl, $CaCO_3$;

dissociation (dissolution) of surface groups, e.g. latex, celluloses, biomolecules, metal oxides (TiO_2);

chemisorption of ions, e.g. phosphates on oxide surfaces;

reaction with OH^- and H^+, e.g. oxide surfaces;

adsorption of ionic surfactants or polyelectrolytes (general – all surfaces);

isomorphous substitution (clay minerals, kaolinite, mica).

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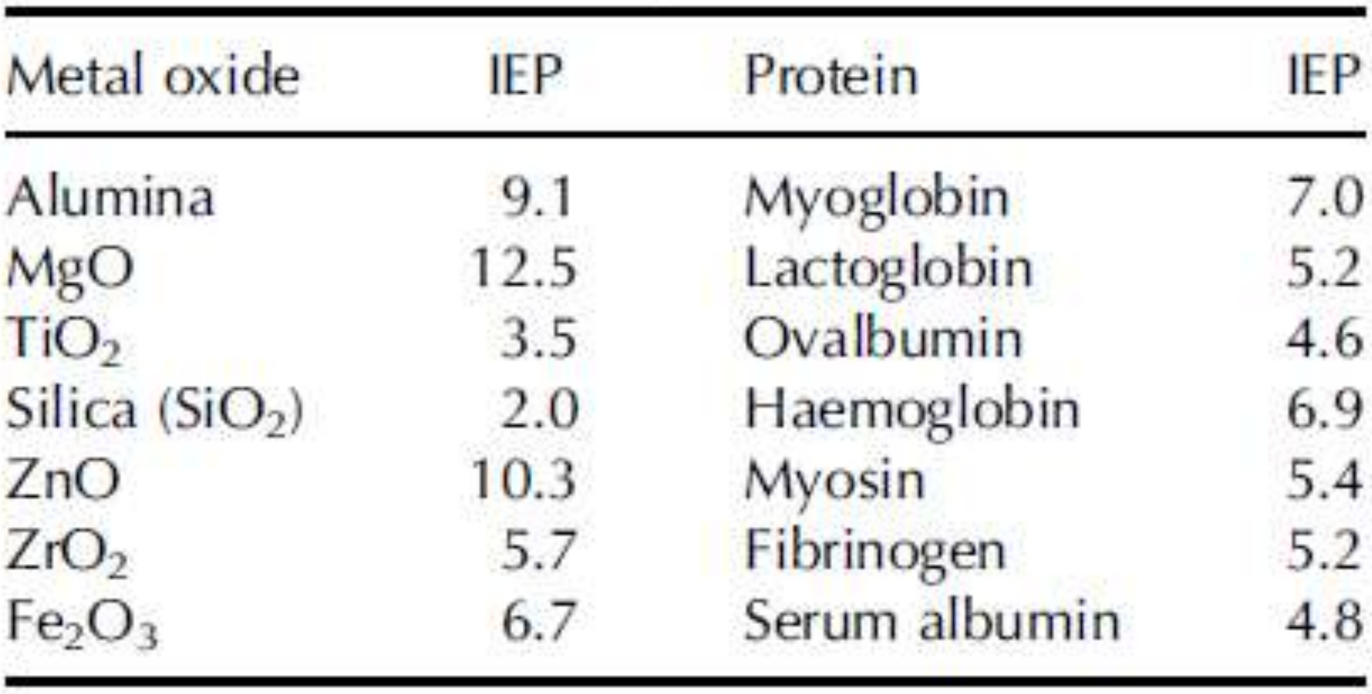
Isoelectric point (IEP) also called the point of zero charge (PZC)



Metal oxide	IEP	Protein	IEP
Alumina	9.1	Myoglobin	7.0
MgO	12.5	Lactoglobin	5.2
TiO_2	3.5	Ovalbumin	4.6
Silica (SiO_2)	2.0	Haemoglobin	6.9
ZnO	10.3	Myosin	5.4
ZrO_2	5.7	Fibrinogen	5.2
Fe_2O_3	6.7	Serum albumin	4.8

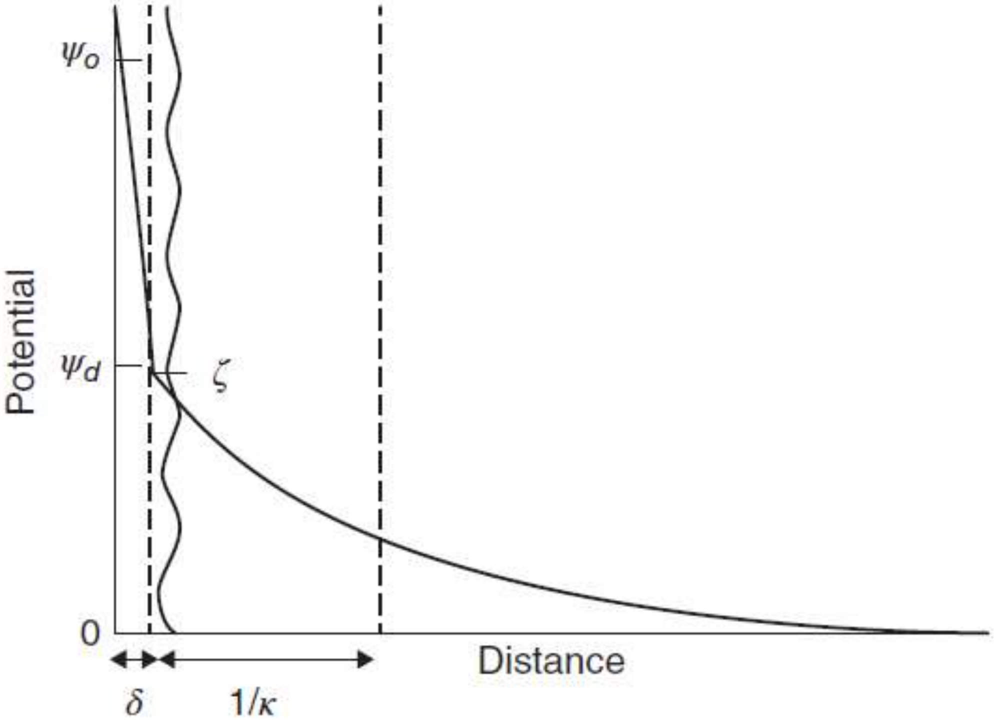
Electrical forces: key parameters (Debye length and zeta potential)

The Debye length „ κ^{-1}" (or screening length) is a measure of the length (thickness) of the double layer and depends on the solvent, temperature and the ionic strength of the solution.

The potential energy of repulsive forces decreases exponentially with the distance and increases with increasing Debye length, relative permittivity and surface potential.

The surface potential „ ψ_o" is approximated by the so called zeta potential „ζ".

Surface or zeta potential and electrophoretic experiments



The zeta potential can also be defined as the potential where the centre of the first layer of solvated ions moving relative to the surface is located.

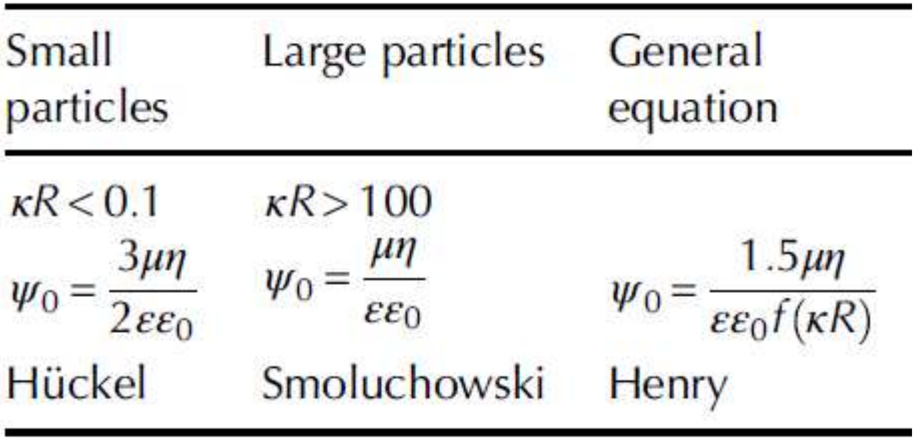
Goodwin (2009) states that this is about 0.5 nm or so from the surface.

A rule of thumb often cited suggests that the absolute value of the zeta potential, for stability in many practical situations, should be larger than 30 mV.

Hückel Smoluchowski and Henry equation

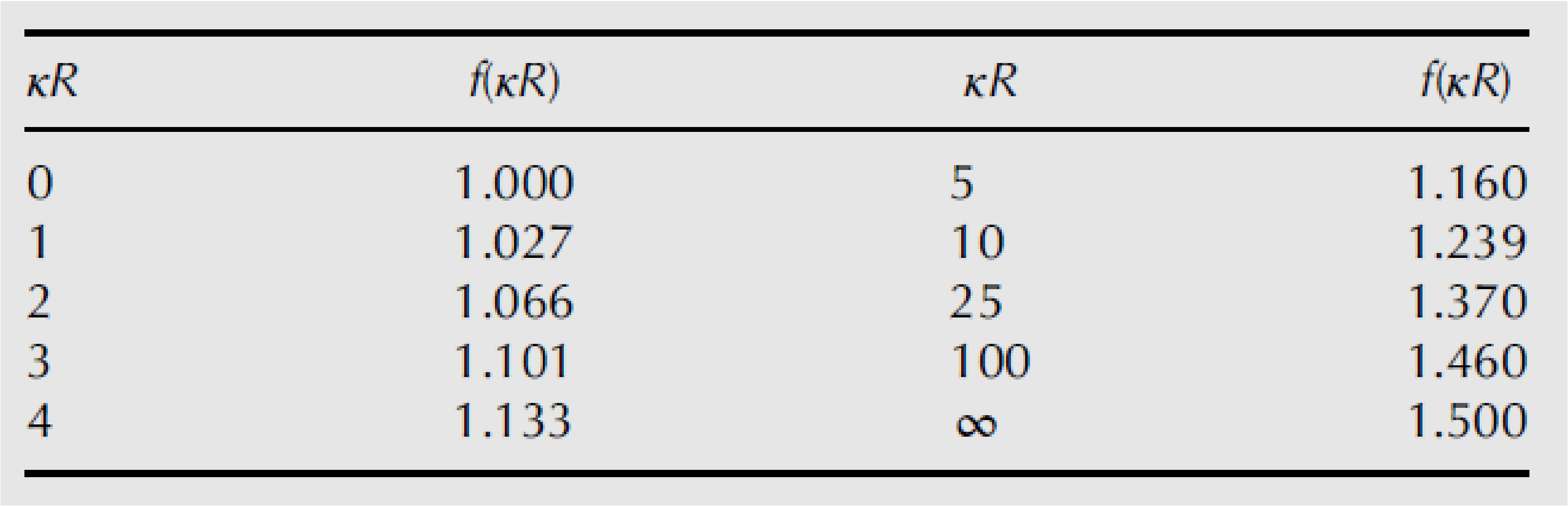
The zeta potential is much lower than the Stern potential in those cases where we have high potential and high salt concentrations.

- The limiting cases of very small (Hückel) and very large (Smoluchowski) particles, which correspond to the point charge and flat surfaces assumptions, respectively.
- “Approximate” equations, like the Henry equation, which are valid also in the intermediate range, are useful.



Small particles	Large particles	General equation
$\kappa R<0.1$	$\kappa R>100$	
$\psi_0=\frac{3\mu\eta}{2\varepsilon\varepsilon_0}$	$\psi_0=\frac{\mu\eta}{\varepsilon\varepsilon_0}$	$\psi_0=\frac{1.5\mu\eta}{\varepsilon\varepsilon_0 f(\kappa R)}$
Hückel	Smoluchowski	Henry

The f correction parameter of the Henry equation for various values of κR



κR	$f(\kappa R)$	κR	$f(\kappa R)$
0	1.000	5	1.160
1	1.027	10	1.239
2	1.066	25	1.370
3	1.101	100	1.460
4	1.133	∞	1.500

Variation of zeta potential with both pH and salt concentration

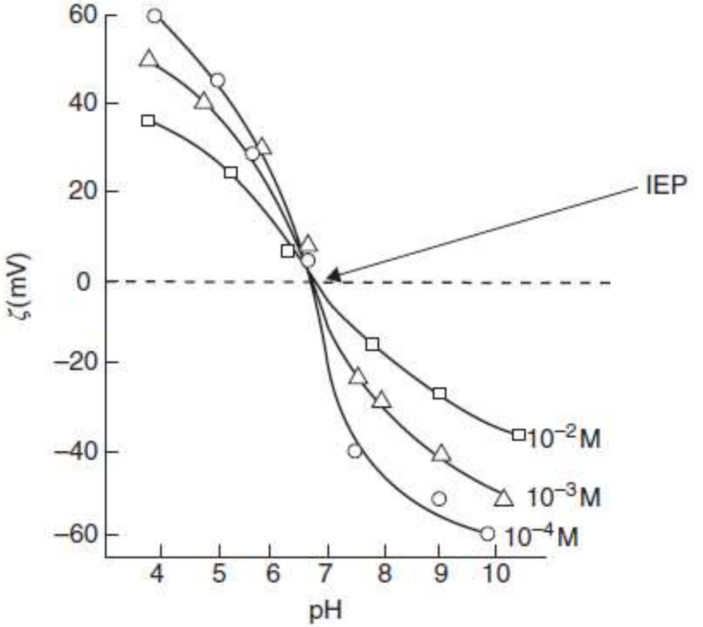


Figure 10.13 The zeta potential decreases with increasing salt concentration and thus salts enhance instability in two ways (also by decreasing the Debye or double layer thickness). The isoelectric point, IEP, is indicated in the figure. Adapted from Hunter (1993), with permission from Oxford University Press

Stability

Stabilization can be obtained if the pH is far from the IEP and/or upon adding small charged molecules that adsorb to the surface, e.g. citric acid or upon adding polymers (block-copolymers, polyelectrolytes).

When the zeta potential is zero (at the IEP), there is no charge on the particles and flocculation will take place.

How to reverse the sign of the zeta potential?

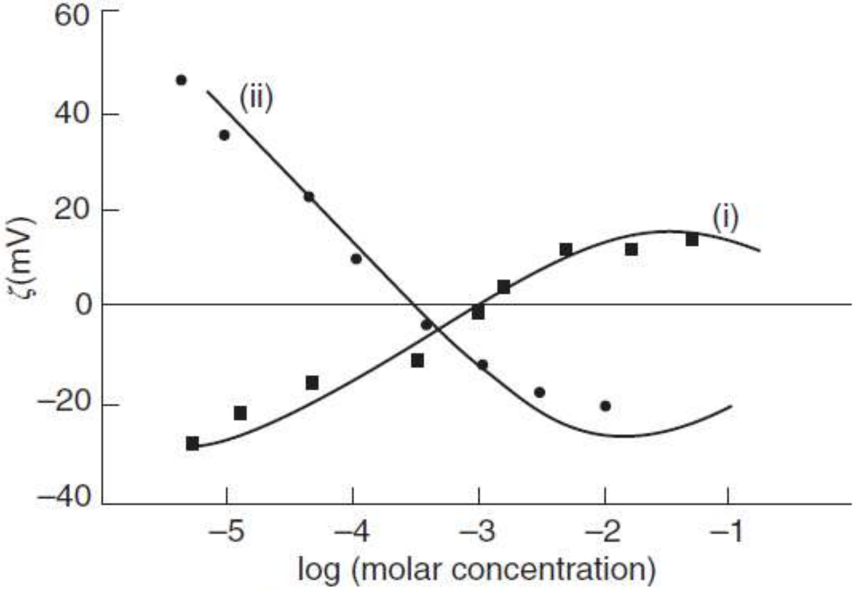
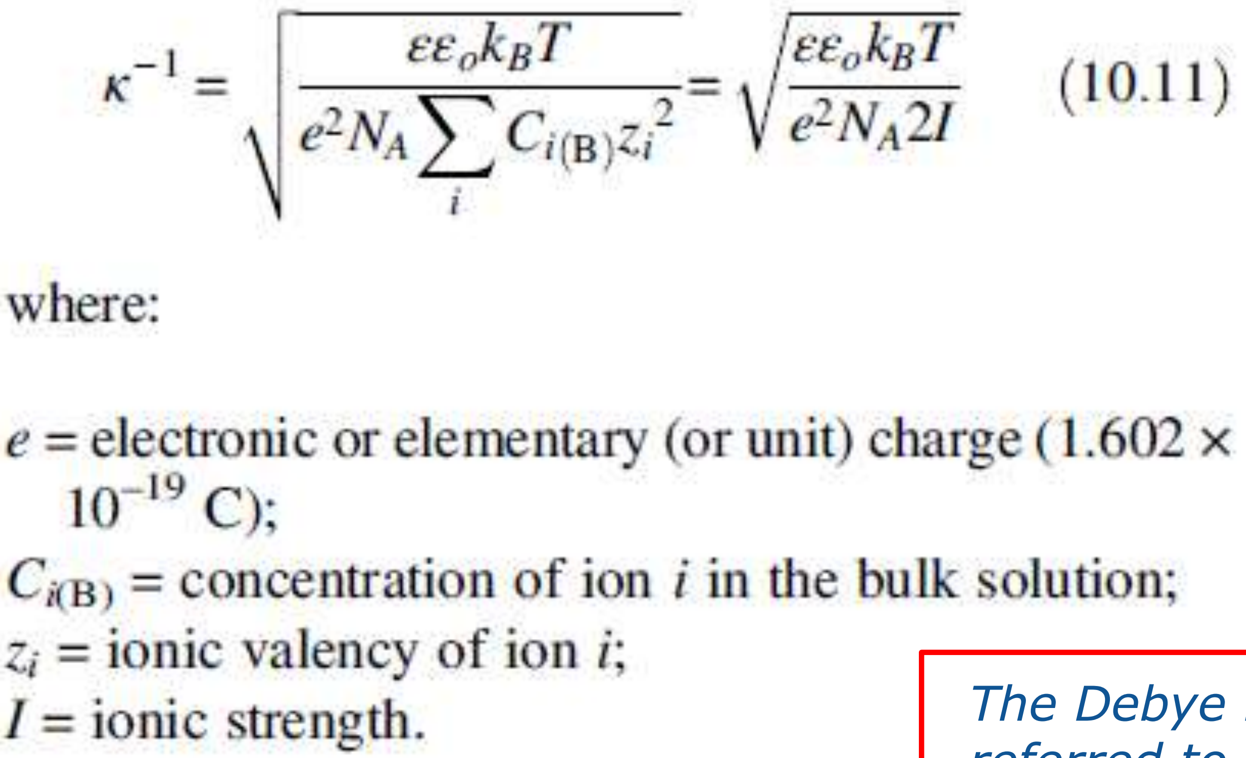


Figure 10.15 *Zeta potential (ζ) of alumina particles under different conditions: (i) negatively charged* Al_2O_3 *(at pH 10) in the presence of* $BaCl_2$*; (ii) positively charged* Al_2O_3 *(at pH 6.5 in the presence of* Na_2SO_4*). The x-axis shows the concentration of* $BaCl_2$ *or* Na_2SO_4*. Hunter (1993), with permission from Oxford University Press*



$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_o k_B T}{e^2 N_A \sum_i C_{i(\mathrm{B})} z_i^2}} = \sqrt{\frac{\varepsilon\varepsilon_o k_B T}{e^2 N_A 2I}} \qquad (10.11)$$

where:

e = electronic or elementary (or unit) charge (1.602×10^{-19} C);
$C_{i(\mathrm{B})}$ = concentration of ion i in the bulk solution;
z_i = ionic valency of ion i;
I = ionic strength.

The Debye length, κ^{-1}, is often referred to as the "thickness of the double layer" even though the region of varying potential is of the order of $3/\kappa$ to $4/\kappa$ (Hunter, 1993).

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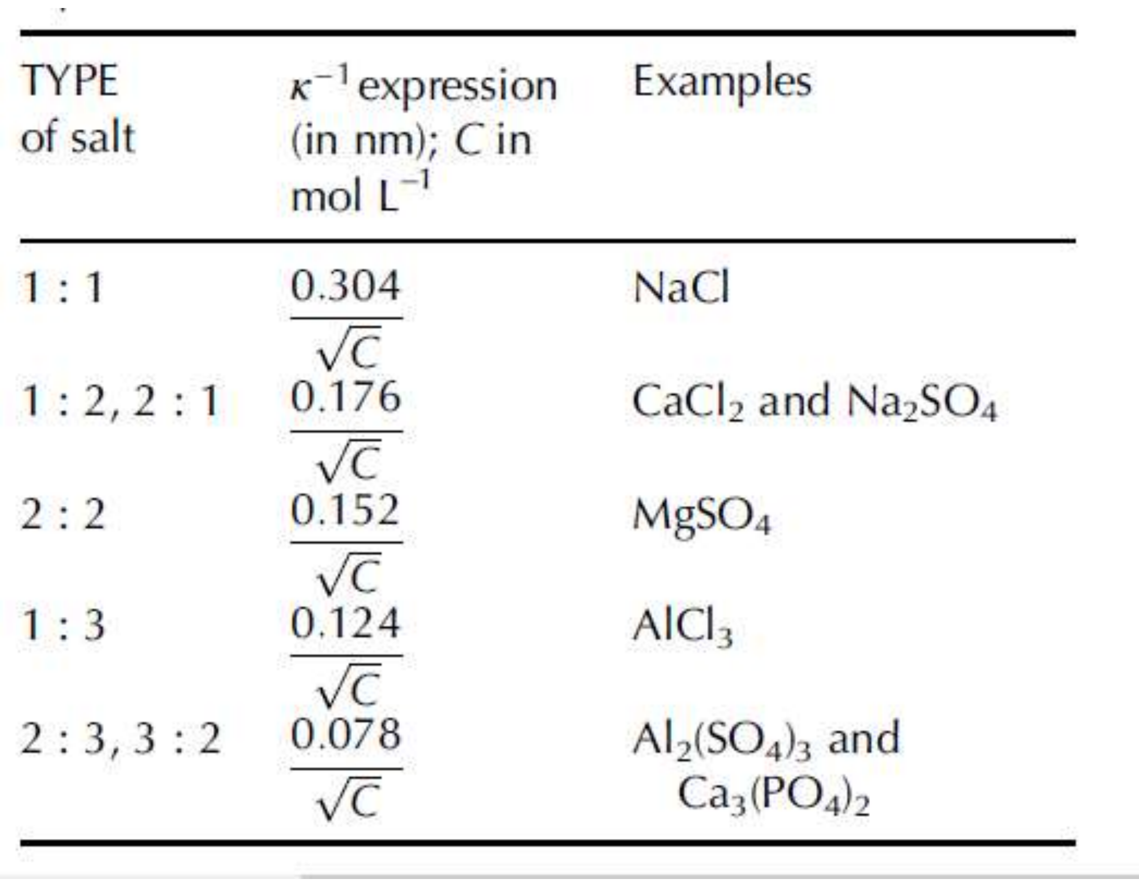
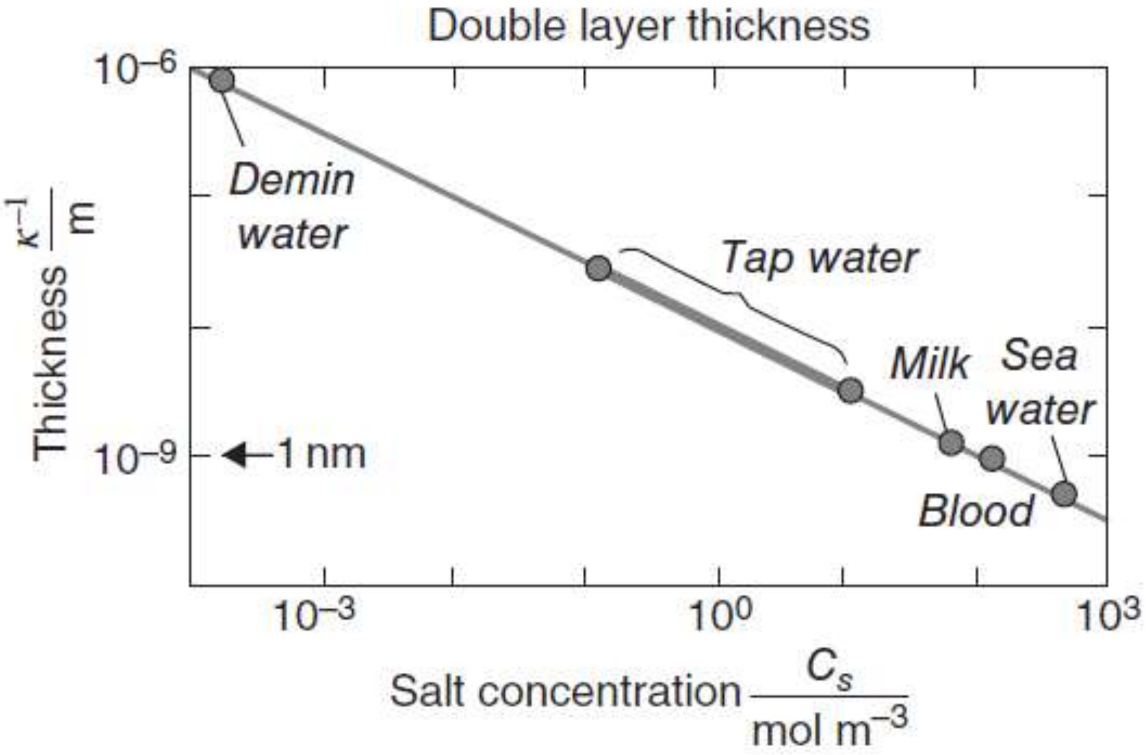
Debye length for aqueous solutions for different types of salts



TYPE of salt	κ^{-1} expression (in nm); C in mol L^{-1}	Examples
1 : 1	$\frac{0.304}{\sqrt{C}}$	NaCl
1 : 2, 2 : 1	$\frac{0.176}{\sqrt{C}}$	$CaCl_2$ and Na_2SO_4
2 : 2	$\frac{0.152}{\sqrt{C}}$	$MgSO_4$
1 : 3	$\frac{0.124}{\sqrt{C}}$	$AlCl_3$
2 : 3, 3 : 2	$\frac{0.078}{\sqrt{C}}$	$Al_2(SO_4)_3$ and $Ca_3(PO_4)_2$

Double layer thickness–salt relationship for water



The dependence of the double-layer thickness on both the electrolyte concentration and type

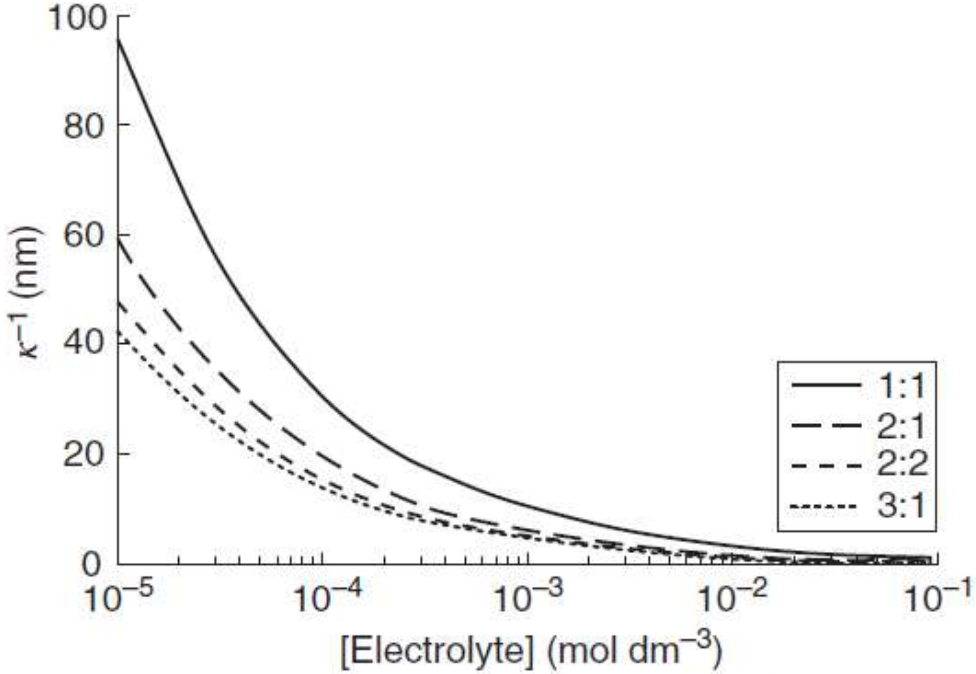


Figure 10.17 *Debye–Hückel decay length as a function of salt concentration for various types of salts. Reprinted from Goodwin (2009), with permission from John Wiley & Sons, Ltd*

Electrical forces

When two charged particles approach each other, their double layers begin to overlap, and they repel each other.

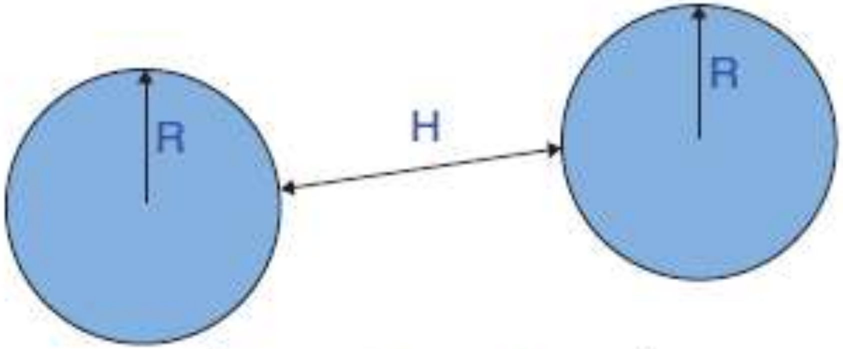
The force falls exponentially with distance and with decreasing Debye length.

It is effectively zero after a few times the thickness of the double layer.

Decreases less rapidly with distance compared to the vdW forces.

Electrostatic double-layer interactions and the simplest mathematical expression

Equation is valid for monodisperse spherical colloidal particles when the so-called Debye–Hückel approximation is fulfilled and when $\kappa R < 5$.

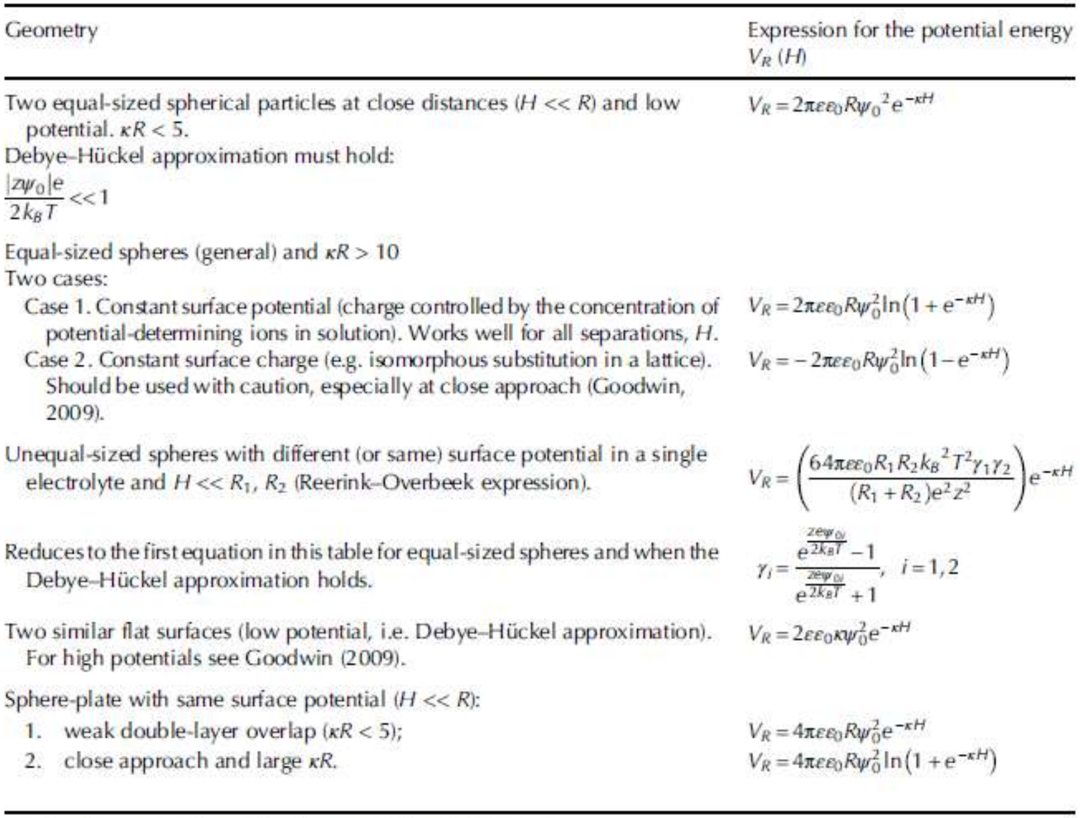


$$\boxed{V_R = 2\pi R \varepsilon_0 \varepsilon \psi_0^2 e^{-\kappa H}}$$

$$\frac{|z\psi_o|e}{2k_B T} \ll 1$$

The Debye–Hückel approximation (strictly valid when a single symmetrical electrolyte (e.g. 1 : 1 or 2:2))

Approximate expressions for the potential energy of electrostatic interactions, V_R



Geometry	Expression for the potential energy $V_R\,(H)$
Two equal-sized spherical particles at close distances ($H << R$) and low potential. $\kappa R < 5$. Debye–Hückel approximation must hold: $\frac{\lvert z\psi_0 \rvert e}{2k_BT} << 1$	$V_R = 2\pi\varepsilon\varepsilon_0 R{\psi_0}^2 e^{-\kappa H}$
Equal-sized spheres (general) and $\kappa R > 10$ Two cases:	
Case 1. Constant surface potential (charge controlled by the concentration of potential-determining ions in solution). Works well for all separations, H.	$V_R = 2\pi\varepsilon\varepsilon_0 R\psi_0^2 \ln\left(1 + e^{-\kappa H}\right)$
Case 2. Constant surface charge (e.g. isomorphous substitution in a lattice). Should be used with caution, especially at close approach (Goodwin, 2009).	$V_R = -2\pi\varepsilon\varepsilon_0 R\psi_0^2 \ln\left(1 - e^{-\kappa H}\right)$
Unequal-sized spheres with different (or same) surface potential in a single electrolyte and $H << R_1$, R_2 (Reerink–Overbeek expression).	$V_R = \left(\frac{64\pi\varepsilon\varepsilon_0 R_1 R_2 {k_B}^2 T^2 \gamma_1 \gamma_2}{(R_1 + R_2) e^2 z^2}\right) e^{-\kappa H}$
Reduces to the first equation in this table for equal-sized spheres and when the Debye–Hückel approximation holds.	$\gamma_i = \frac{e^{\frac{ze\psi_{0i}}{2k_BT}} - 1}{e^{\frac{ze\psi_{0i}}{2k_BT}} + 1}, \quad i = 1,2$
Two similar flat surfaces (low potential, i.e. Debye–Hückel approximation). For high potentials see Goodwin (2009).	$V_R = 2\varepsilon\varepsilon_0 \kappa \psi_0^2 e^{-\kappa H}$
Sphere-plate with same surface potential ($H << R$):	
1. weak double-layer overlap ($\kappa R < 5$);	$V_R = 4\pi\varepsilon\varepsilon_0 R\psi_0^2 e^{-\kappa H}$
2. close approach and large κR.	$V_R = 4\pi\varepsilon\varepsilon_0 R\psi_0^2 \ln\left(1 + e^{-\kappa H}\right)$

Data from Shaw (1992), from Israelachvili (2011) and from Goodwin (2009).

Born repulsion

At very short distances of approach Ångstrøms), H, there can be overlap of molecular orbitals.

This is known as Born repulsion and these interactions are very short-range (proportional to H^{-12}*).*

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Schulze–Hardy rule and the critical coagulation concentration (CCC)

The critical coagulation concentration, often abbreviated as CCC, is the minimum concentration of an (inert) electrolyte that is just sufficient to coagulate a dispersion.

The CCC depends only very weakly on factors other than the counter-ion valency (like the charge number of co-ions and the concentration of the particle, and even moderately on the nature of the particle itself).

All these generalizations are known as the Schulze–Hardy rule.

Small amounts af salt can reduce drastically the stability of colloids

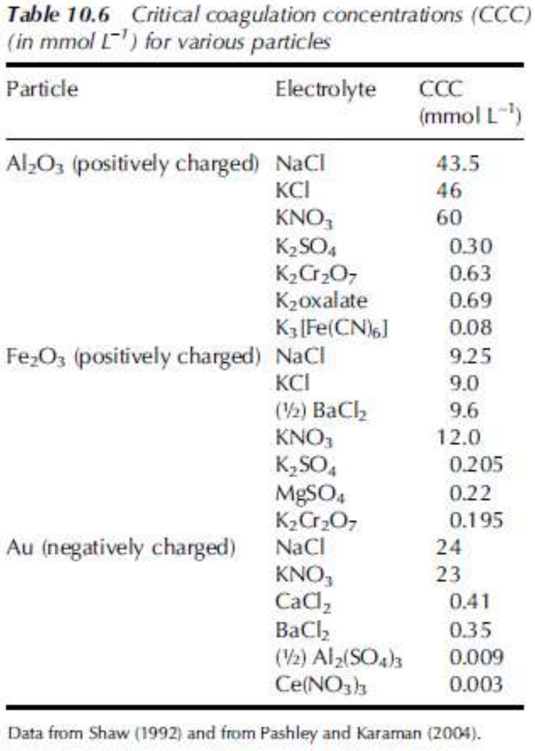
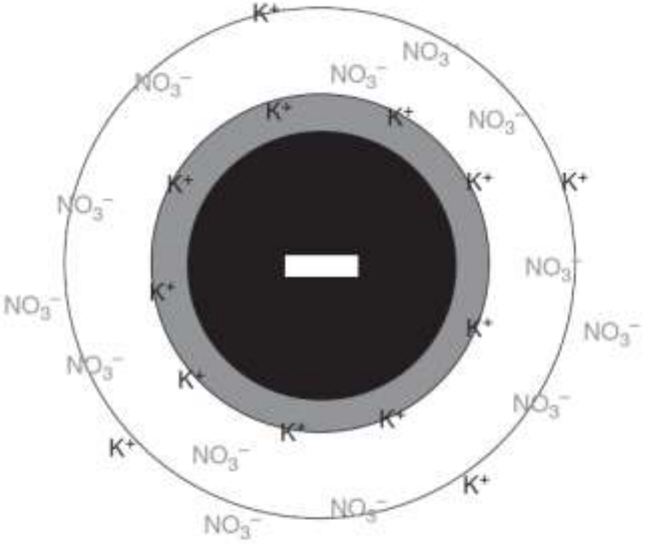


Table 10.6 *Critical coagulation concentrations (CCC) (in mmol L^{-1}) for various particles*

Particle	Electrolyte	CCC (mmol L^{-1})
Al_2O_3 (positively charged)	NaCl	43.5
	KCl	46
	KNO_3	60
	K_2SO_4	0.30
	$K_2Cr_2O_7$	0.63
	K_2oxalate	0.69
	$K_3[Fe(CN)_6]$	0.08
Fe_2O_3 (positively charged)	NaCl	9.25
	KCl	9.0
	(½) $BaCl_2$	9.6
	KNO_3	12.0
	K_2SO_4	0.205
	$MgSO_4$	0.22
	$K_2Cr_2O_7$	0.195
Au (negatively charged)	NaCl	24
	KNO_3	23
	$CaCl_2$	0.41
	$BaCl_2$	0.35
	(½) $Al_2(SO_4)_3$	0.009
	$Ce(NO_3)_3$	0.003

Data from Shaw (1992) and from Pashley and Karaman (2004).



$$CCC \propto \frac{1}{z^6} \Rightarrow CCC(salt\ II) = CCC(salt\ I)\left(\frac{z_I}{z_{II}}\right)^6$$

Figure 10.19 *The role of salt in colloid stability as described via the Schulze–Hardy rule for dispersions. The critical coagulation concentration (CCC) is inversely proportional to z^6 (the exponent 6 is an average value and a reasonable number to use). This fact leads to the equation in the figure for two salts with different ionic valencies (i.e. one can calculate the CCC of one salt from CCC of another salt with a different counter-ion valency). In the drawing, the particle is negatively charged (e.g. a AgI particle), K^+ is the counter-ion and NO_3^- is the co-ion*

Concluding remarks: vdW forces

they are long-range and extremely strong – much longer range than the vdW forces between molecules;

they are almost always attractive and thus contribute to instability;

they are always attractive in air and in vacuum (where the Hamaker constant is zero);

they are always attractive between two identical surfaces or particles;

they depend on the size/shape, in general the geometry of the particles (e.g. spherical, flat surfaces or cylindrical); thus there are several analytical expressions for the van der Waals forces;

they depend on the material and the medium (via the Hamaker constant);

they decrease because of an intervening medium (this can help in controlling the vdW forces!, e.g. by changing the solvent or adding a layer containing a large amount of the solvent);

they are weak if particles and medium are chemically similar;

they can be repulsive (sometimes) between different surfaces (or particles) in a medium (if the Hamaker constant of the medium has a value intermediate to those of the particles, which means that one material interacts more strongly with the medium than with the second body).

Concluding remarks: Electrostatic/electric forces

decrease with increasing distance exponentially (and this is a different dependency than for the vdW attractive forces);

depend on the size of particles (or surfaces);

depend on the medium (often water);

depend on the surface (potential) – zeta potential;

depend on the electrolyte used (concentration and valency);

are always repulsive between identical surfaces but they can be attractive between dissimilar surfaces

The Debye length

It is a length (usually in nm) – a measure of the thickness of double layer.

It depends on both electrolyte type and concentration.

It decreases with increasing salt concentration.

It "protects" – it helps stability! We want the Debye thickness to be as high as possible for good stability!

The diffuse double layer fades away at a distance 2–3 times the Debye length.

For understanding electrical forces we recall the following steps:

identify the source of surface charge;

measure surface charge (zeta potential) versus pH;

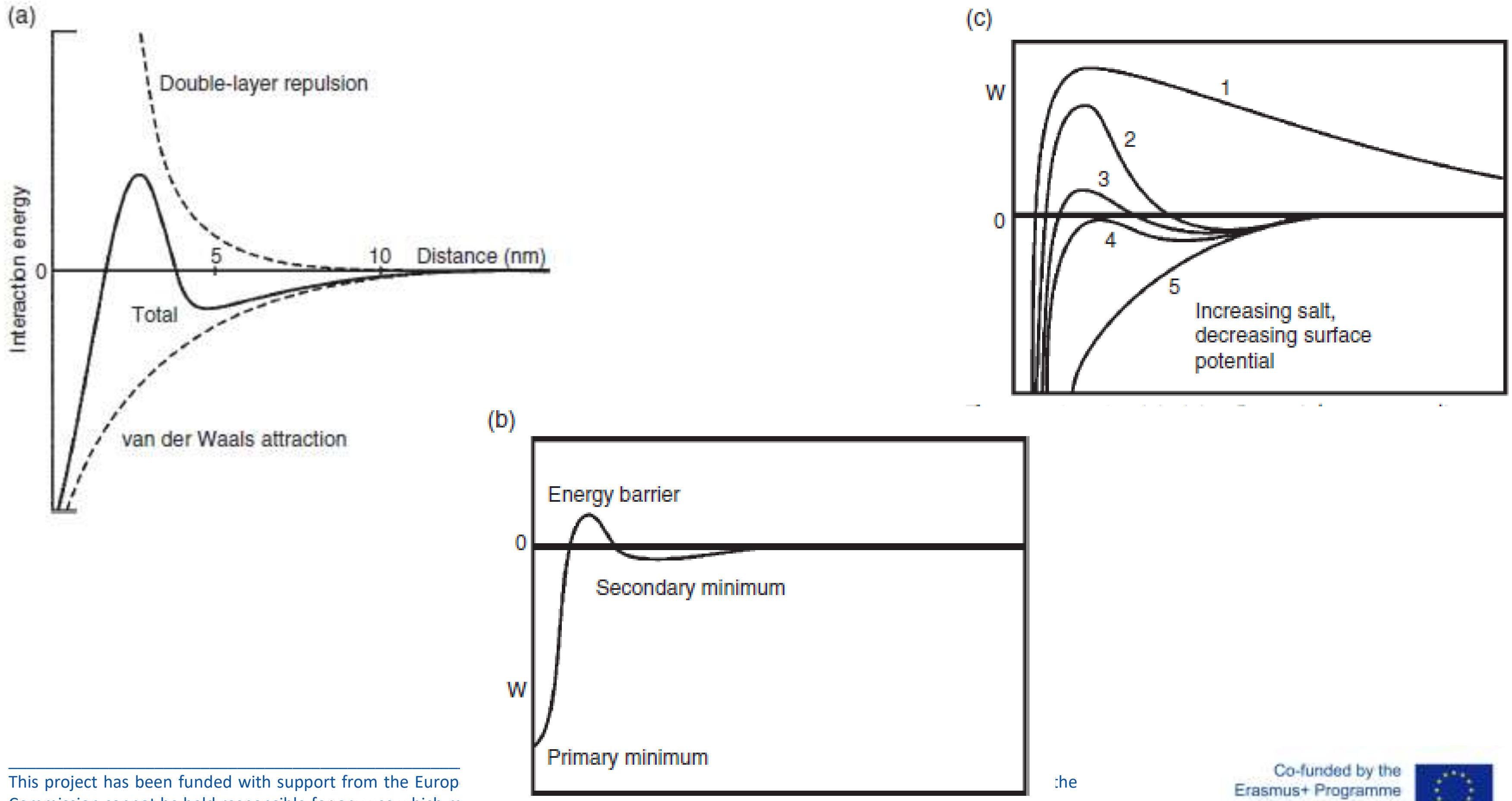
regulate surface charge (and via this the diffuse double layer), e.g. ion adsorption, adsorption of polymers especially polyelectrolytes, proteins, (ionic) surfactants, small charged molecules, surface treatment (curing, chemical modification) –pH and common ions can help in controlling the surface charge;

stability is obtained far from pH = IEP and far

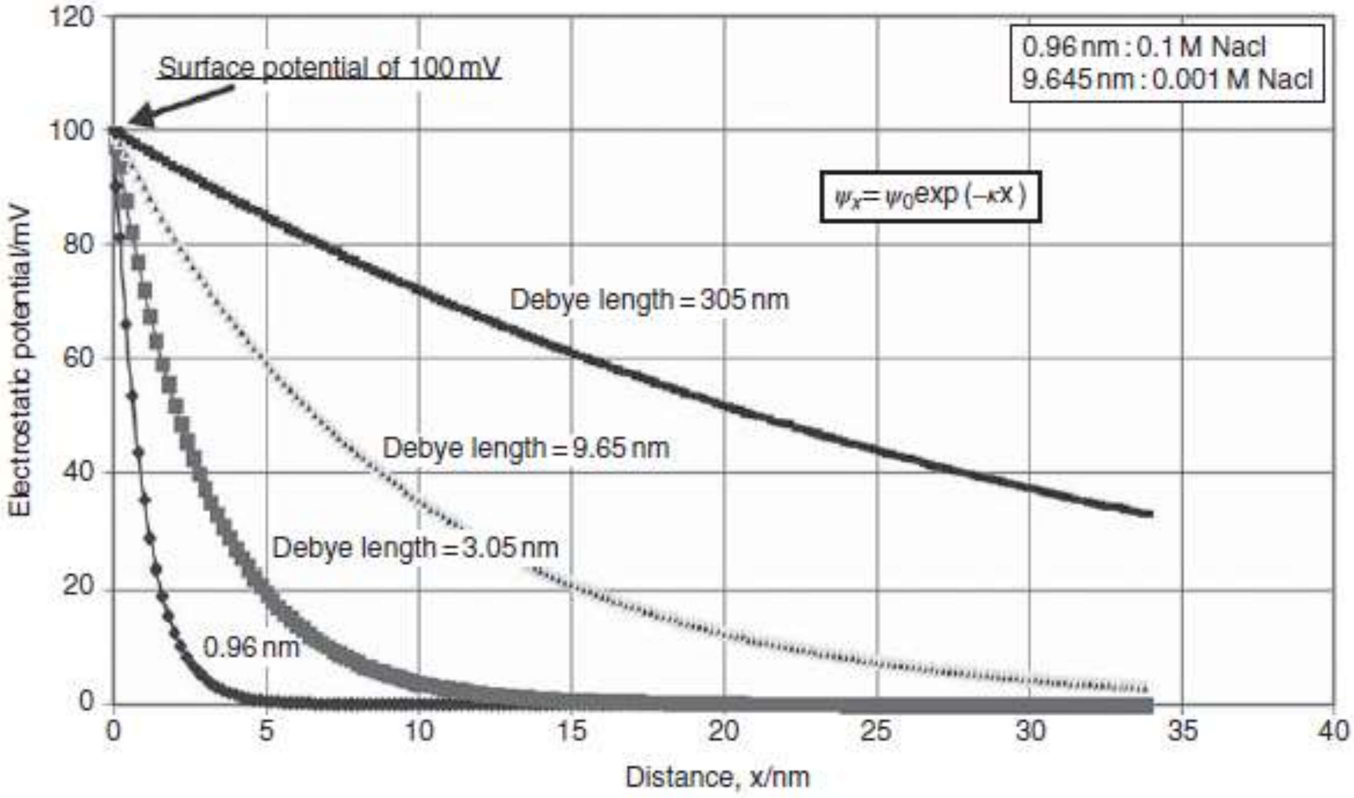
from the point of zero charge (PZC);

control salt content, temperature and medium.

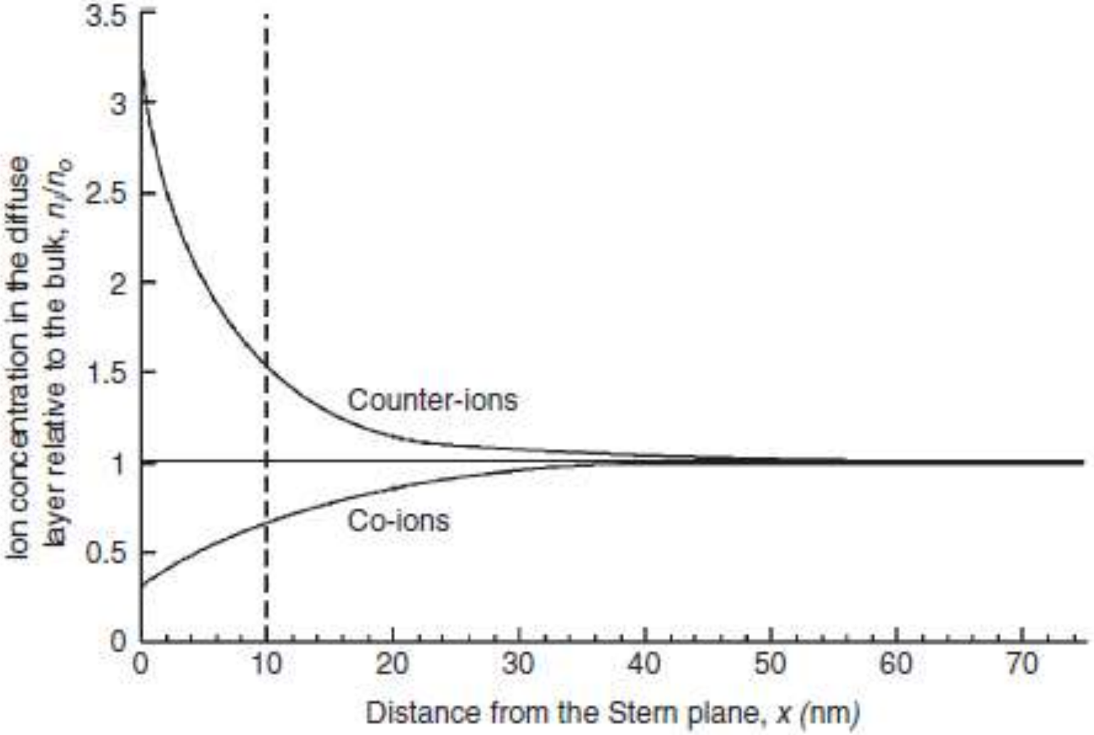
Which colloid is the most stable?



Stability?


Surface potential of 100 mV
0.96 nm : 0.1 M Nacl
9.645 nm : 0.001 M Nacl
$\psi_x = \psi_0 \exp(-\kappa x)$
Debye length = 305 nm
Debye length = 9.65 nm
Debye length = 3.05 nm
0.96 nm
Electrostatic potential/mV
120
100
80
60
40
20
0
0
5
10
15
20
25
30
35
40
Distance, x/nm

Ion concentration outside the double layer



Stability of particles in different solvents

The maximum stability is observed in moderately polar solvents (with relative permittivities between 20 and 45).

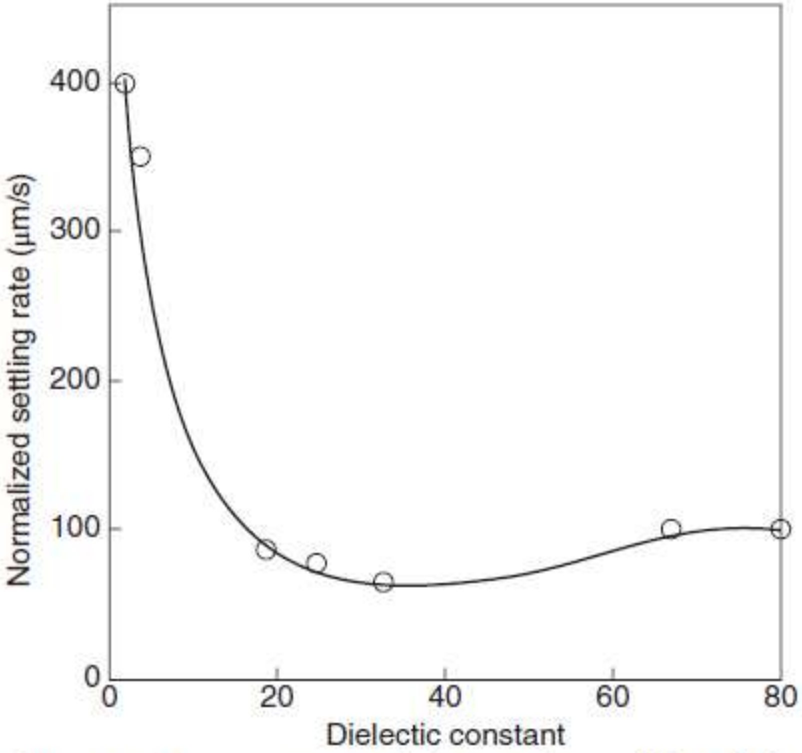


Figure 10.24 *Experimental data on the stability of alumina particles in different solvents. The normalized set-*

Author, Editor and Referee References

This remote access laboratory was created thanks to work done primarily at University of Niš.

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Refereeing of this material was done by: ____________________

Editing into NETCHEM Format and onto NETCHEM platform was completed by: Milan Milosevic, Tatjana Andjelkovic

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Surfactants and self-assembly. Detergents and cleaning

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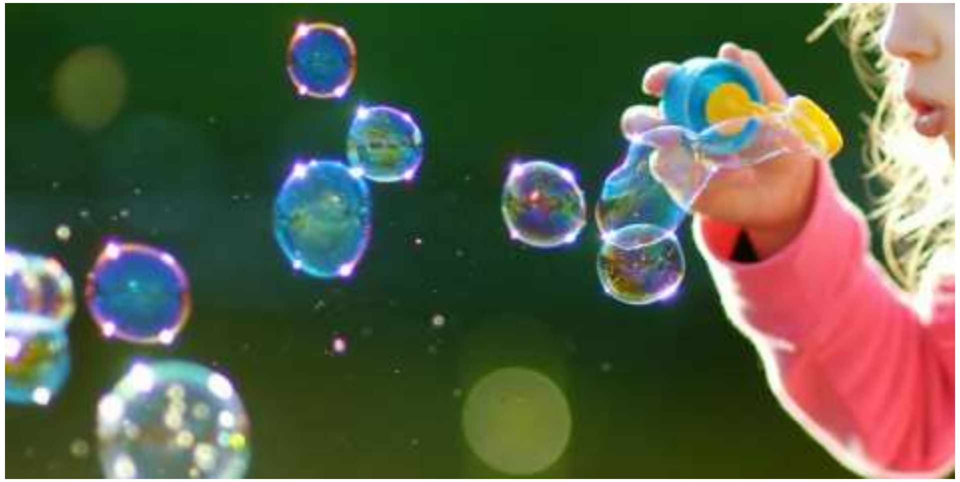
Surface active agents or surfactants



Surfactants are amphiphilic compounds, consisting of a "polar" head (ionic –anionic or cationic - or polar group) and a hydrophobic part.

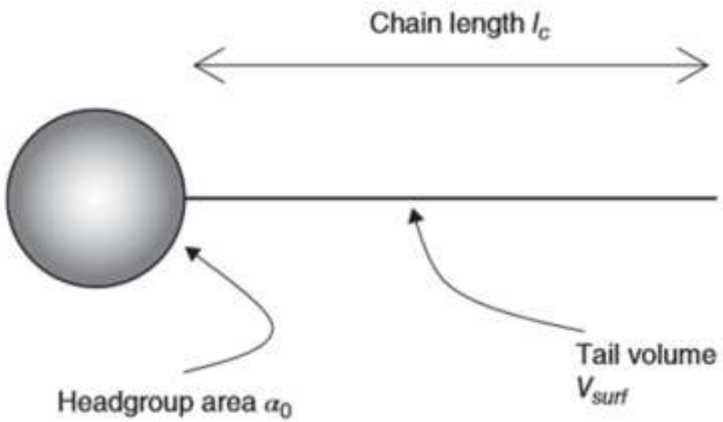
Surfactants adsorb on liquid–air and oil–water interfaces and decrease surface and interfacial tensions and the corresponding works of adhesion.

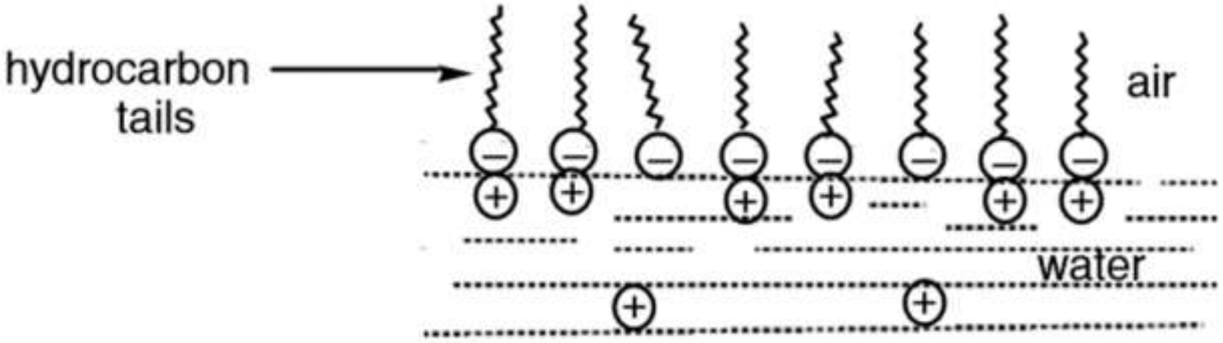
Water molecules surrounding the hydrocarbon groups order, so as to increase the number of bonds to other neighbouring water molecules (decreasing entropy and increases the free energy).

Basic properties

Important characteristics in surfactant scie include the following parameters:

- **CMC,**
- **Krafft point,**
- **hydrophilic/lipophilic balance,**
- **Temperature,**
- **Salts,**
- **Co-surfactants,**
- **Time.**





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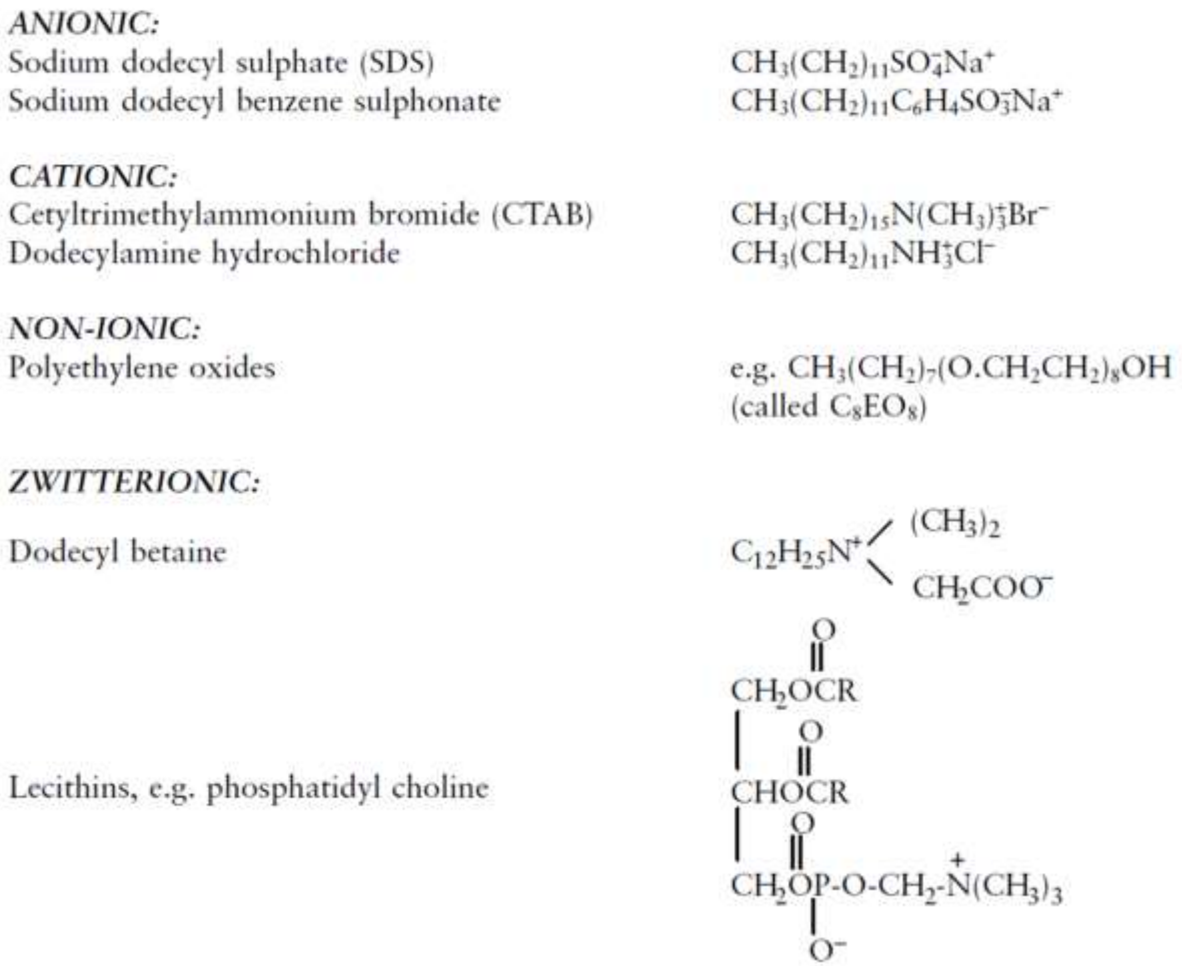
Classification of surfactants

The surfactants can be classified according to the nature of the "head", i.e. their hydrophilic group (anionic, non-ionic, cationic).



ANIONIC:	
Sodium dodecyl sulphate (SDS)	$CH_3(CH_2)_{11}SO_4^-Na^+$
Sodium dodecyl benzene sulphonate	$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$
CATIONIC:	
Cetyltrimethylammonium bromide (CTAB)	$CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$
Dodecylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
NON-IONIC:	
Polyethylene oxides	e.g. $CH_3(CH_2)_7(O.CH_2CH_2)_8OH$ (called C_8EO_8)
ZWITTERIONIC:	
Dodecyl betaine	$C_{12}H_{25}N^+ \langle^{(CH_3)_2}_{CH_2COO^-}$
Lecithins, e.g. phosphatidyl choline	$CH_2OC(=O)R$ – $CHOC(=O)R$ – $CH_2OP(=O)(O^-)$-O-CH_2-$\overset{+}{N}(CH_3)_3$

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Detergents remain the most important use of surfactants

Surfactants have many applications:

- **as important parts of detergents for cleaning,**
- **as emulsifiers,**
- **foaming agents or stabilizers for colloidal dispersions,**
- **in various applications in biotechnology and catalysis,**
- **as components in many complex products, e.g. paints and coatings as well as in lotions, shampoos, etc.**

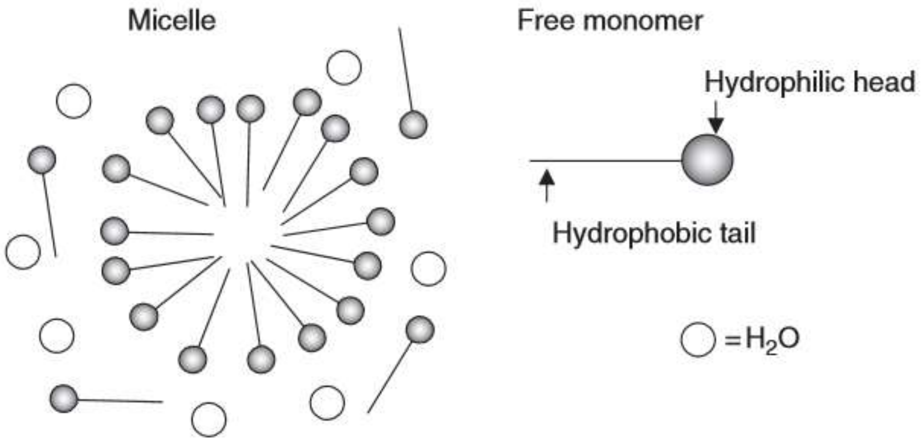
Critical micelle concentration

A decrease of water surface tension is observed up to a certain concentration, called the critical micelle concentration (CMC).

Above the CMC, surfactants create new liquid-like often near spherical structures, called micelles .

Close to CMC micelles are spherical or semi-spherical “liquid-like” aggregates in a very dynamic situation; the life – time of micelles is 1-100ms and the occupancy time of one surfactant in a micelle is 10–1000 µs.

The radius of the micelles is of the order of the length of the surfactant molecules: a few nanometres.

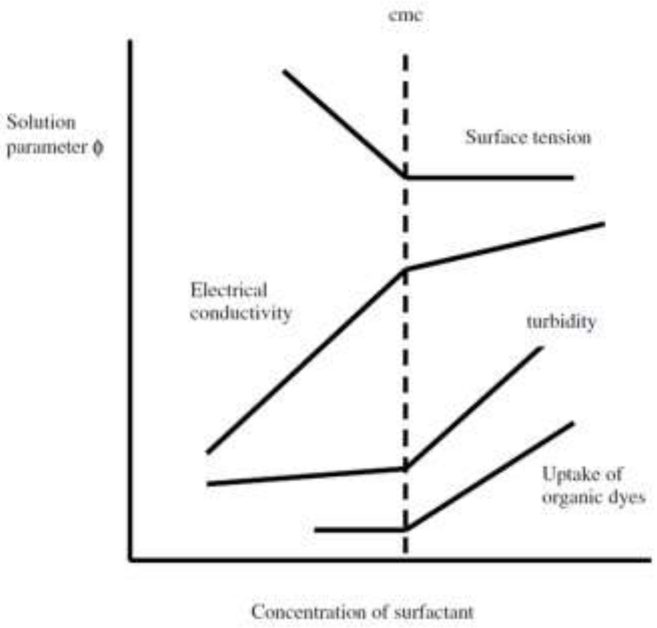


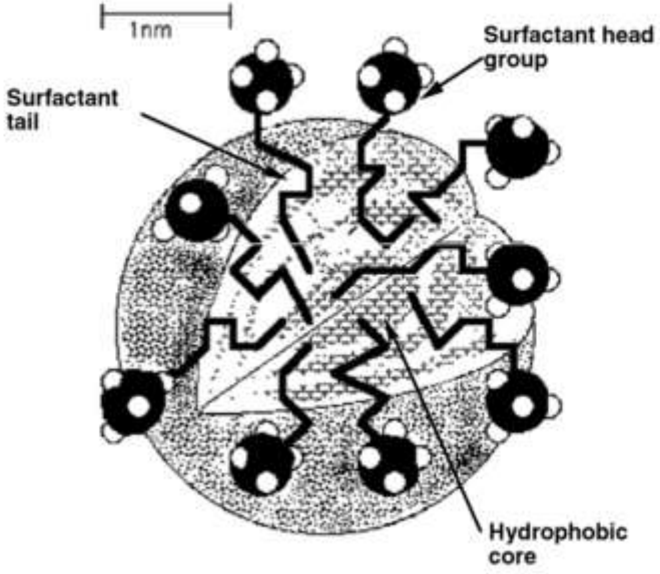
Critical micelle concentration

Some molecules enter the solution but most of them stick on the (water–air) surface.

During this process the surface tension decreases.

When, however, all the surfaces are "saturated" (complete), the surfactants will find other ways to minimize the energy; this happens by the creation of (semi-spherical) liquid-like aggregates, called micelles.





Critical packing parameter (CPP)

A very important characteristic of surfactant molecules, which quantifies their hydrophilic and hydrophobic character, is the so-called CPP (critical packing parameter).

CPP is a geometric parameter of the surfactant defined as

$$\mathrm{CPP} = \frac{V_{surf}}{\alpha_0 l_c}$$

where V_{surf} denotes the tail chain (or chains) volume, lc is the critical tail chain length and a_0 is the headgroup area at the head-tail interface.

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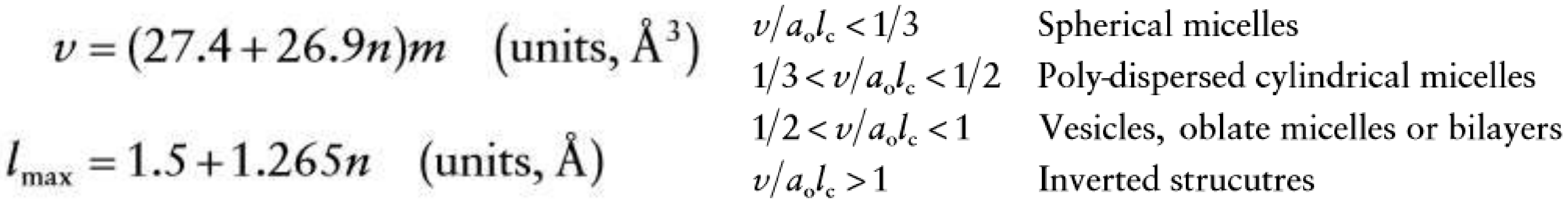
Critical packing parameter (CPP)

The CPP depends significantly on salt, pH, co-surfactant, temperature, counterion, double bonds and double chains.

Approximate expressions for v_{max} *(v) and* l_c *(*l_{max}*) of surfactants as a function of the carbon number chain have been presented*



$$v = (27.4 + 26.9n)m \quad (\text{units, Å}^3)$$

$$l_{\max} = 1.5 + 1.265n \quad (\text{units, Å})$$

$v/a_o l_c < 1/3$	Spherical micelles
$1/3 < v/a_o l_c < 1/2$	Poly-dispersed cylindrical micelles
$1/2 < v/a_o l_c < 1$	Vesicles, oblate micelles or bilayers
$v/a_o l_c > 1$	Inverted strucutres

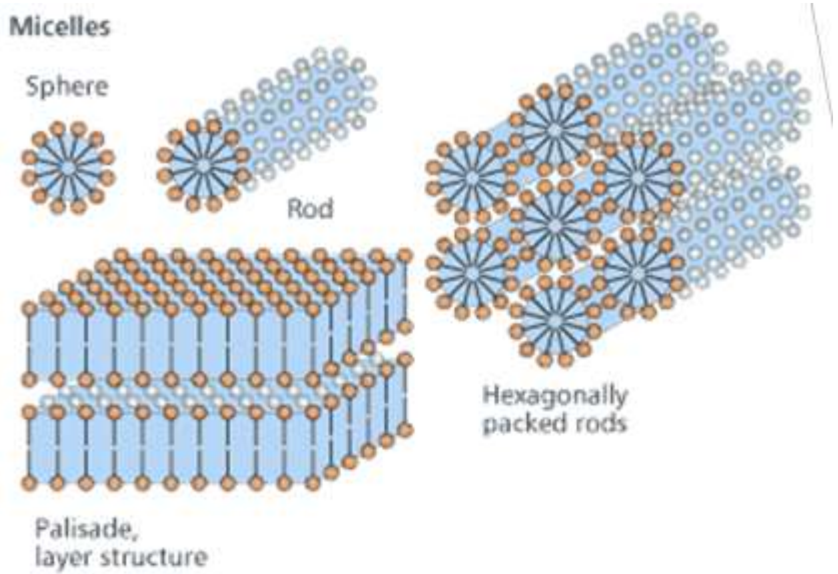
where n is the number of carbon atoms in the hydrocarbon (hydrophobic) chain and m is the number of hydrocarbon (hydrophobic) chains. v is expressed in $Å^3$ *and* l_{max} *is in Å.*

The shape/structure of the micelles

Surfactants having CPP values below 1/3 will create spherical micelles.

Higher CPP values result to other structures

At concentrations higher than CMC, are liquid crystalline structures like hexagonal or lamellar, some of which resemble the structure of biological membranes.



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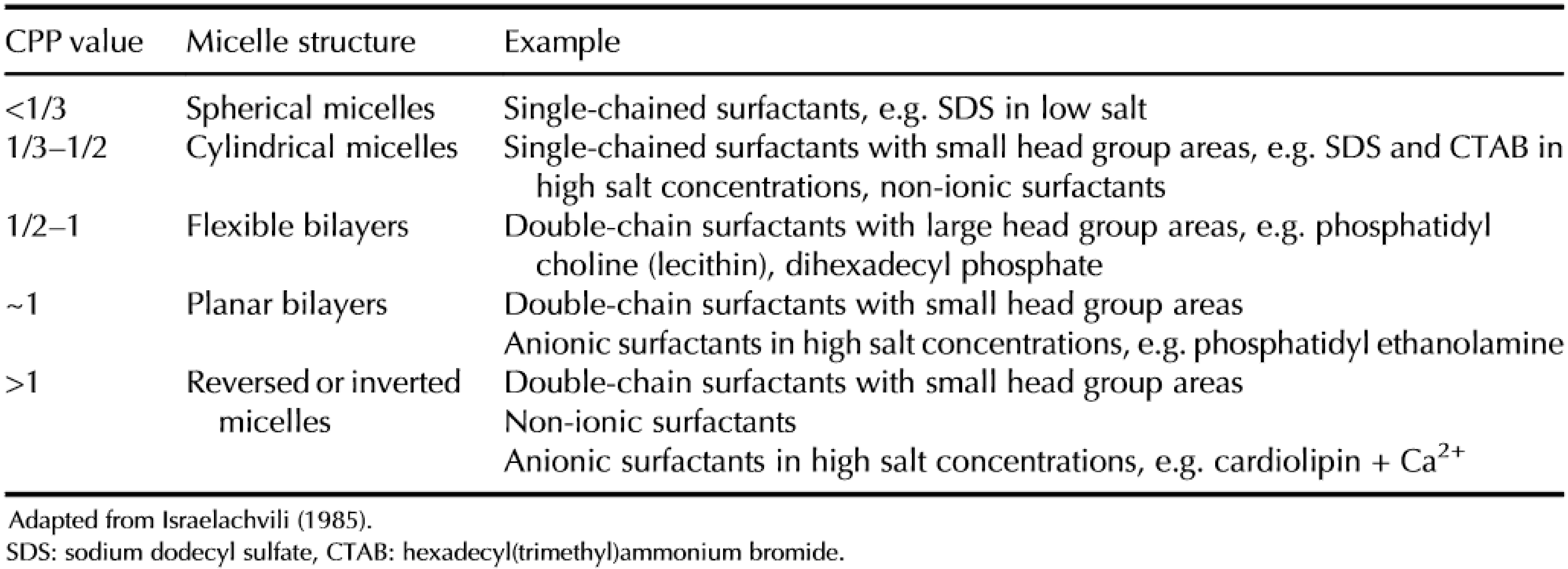
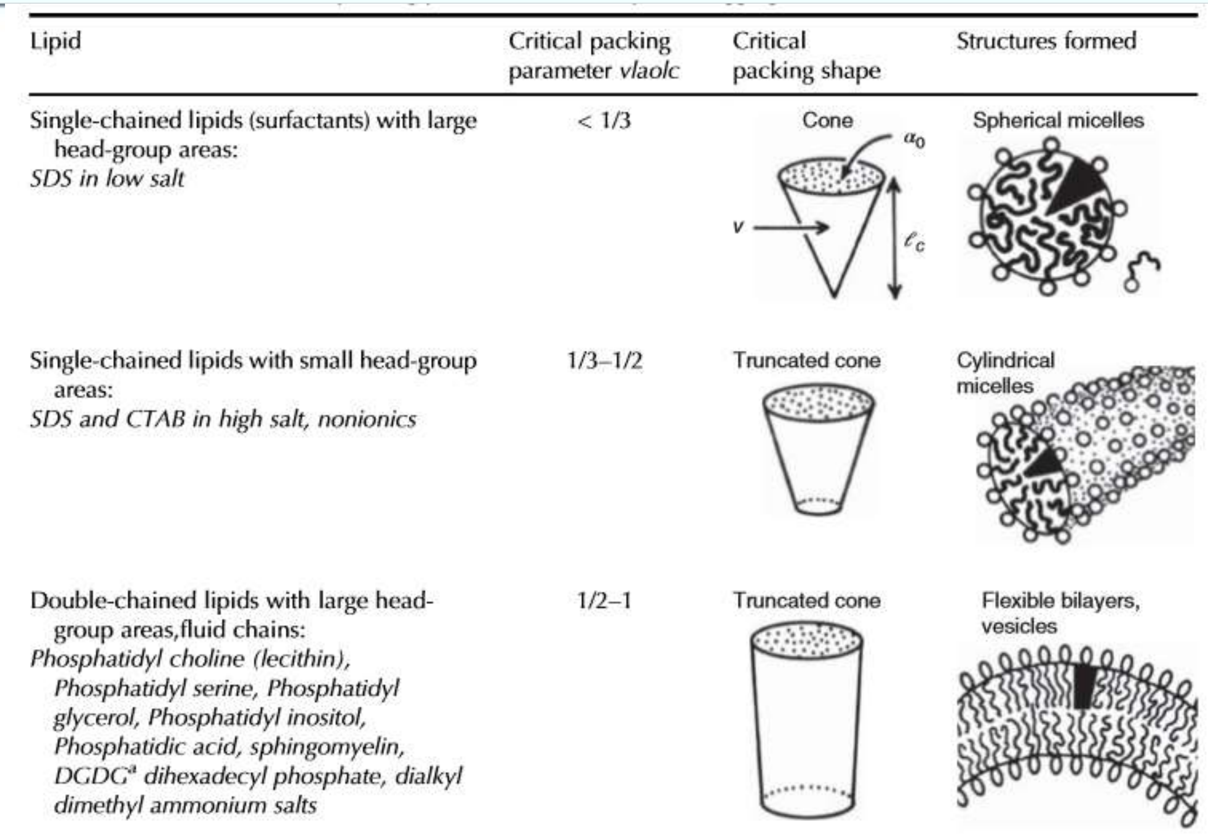
Relationship between CPP values and micelle structure



CPP value	Micelle structure	Example
<1/3	Spherical micelles	Single-chained surfactants, e.g. SDS in low salt
1/3–1/2	Cylindrical micelles	Single-chained surfactants with small head group areas, e.g. SDS and CTAB in high salt concentrations, non-ionic surfactants
1/2–1	Flexible bilayers	Double-chain surfactants with large head group areas, e.g. phosphatidyl choline (lecithin), dihexadecyl phosphate
~1	Planar bilayers	Double-chain surfactants with small head group areas Anionic surfactants in high salt concentrations, e.g. phosphatidyl ethanolamine
>1	Reversed or inverted micelles	Double-chain surfactants with small head group areas Non-ionic surfactants Anionic surfactants in high salt concentrations, e.g. cardiolipin + Ca^{2+}

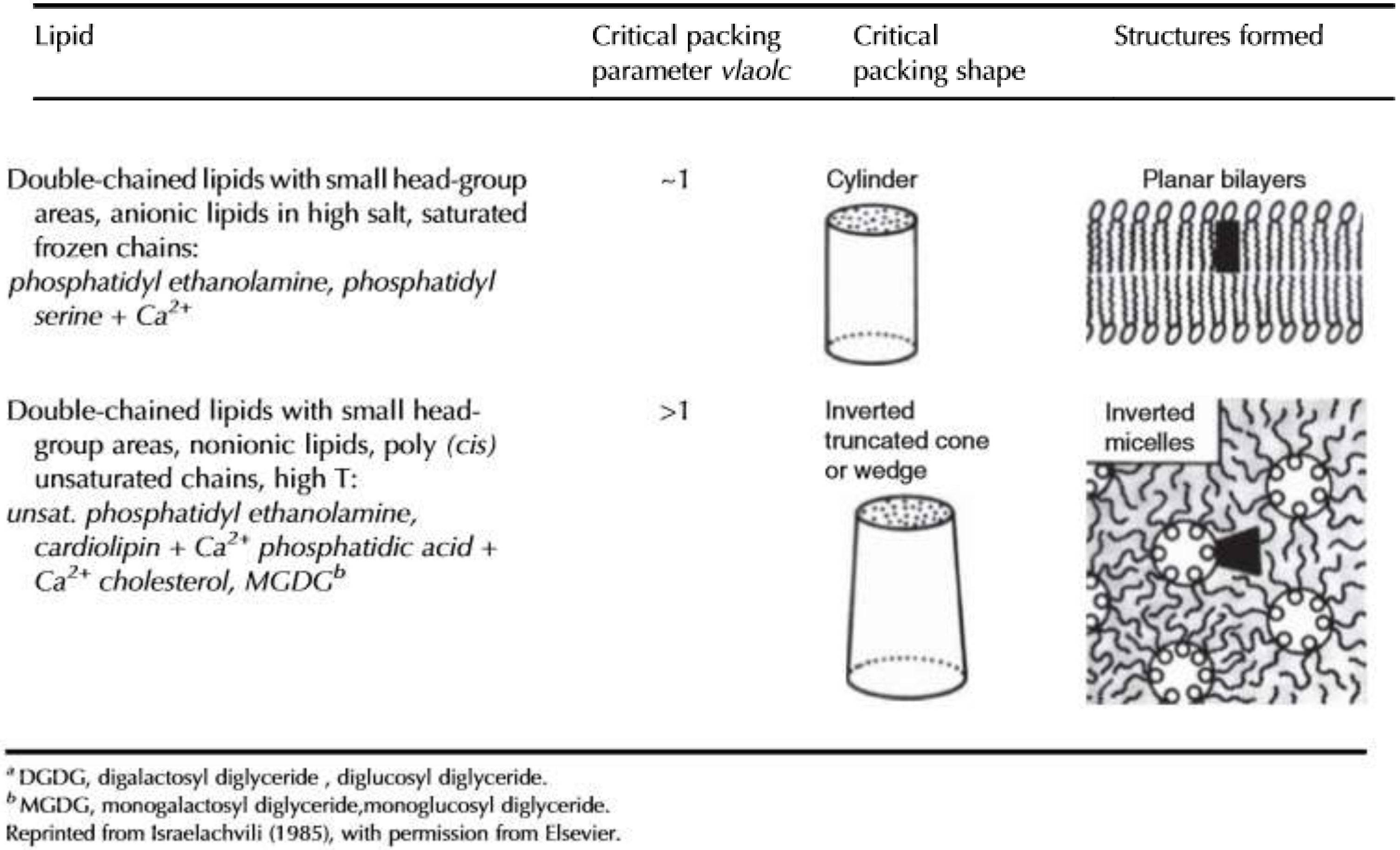
Adapted from Israelachvili (1985).
SDS: sodium dodecyl sulfate, CTAB: hexadecyl(trimethyl)ammonium bromide.

Use of the critical packing parameter (CPP) to predict aggregate structure



Lipid	Critical packing parameter *v/a₀l_c*	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	< 1/3	Cone	Spherical micelles
Single-chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionics*	1/3–1/2	Truncated cone	Cylindrical micelles
Double-chained lipids with large head-group areas, fluid chains: *Phosphatidyl choline (lecithin), Phosphatidyl serine, Phosphatidyl glycerol, Phosphatidyl inositol, Phosphatidic acid, sphingomyelin, DGDG[a] dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2–1	Truncated cone	Flexible bilayers, vesicles

Use of the critical packing parameter (CPP) to predict aggregate structure



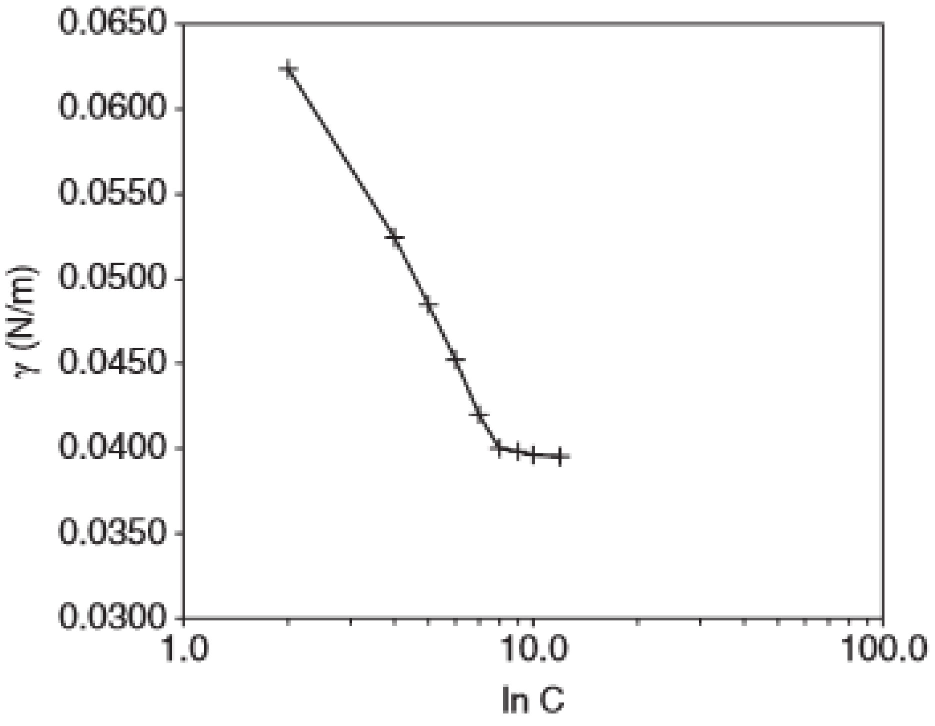
Lipid	Critical packing parameter v/a_0l_c	Critical packing shape	Structures formed
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: *phosphatidyl ethanolamine, phosphatidyl serine* + Ca^{2+}	~1	Cylinder	Planar bilayers
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high T: *unsat. phosphatidyl ethanolamine, cardiolipin* + Ca^{2+} *phosphatidic acid* + Ca^{2+} *cholesterol, MGDG*[b]	>1	Inverted truncated cone or wedge	Inverted micelles

[a] DGDG, digalactosyl diglyceride , diglucosyl diglyceride.
[b] MGDG, monogalactosyl diglyceride,monoglucosyl diglyceride.
Reprinted from Israelachvili (1985), with permission from Elsevier.

Surface tension and CMC

Surface tension (Nm^{-1}) versus logarithm of concentration (C in mol m^{-3}) for an aqueous solution of sodium dodecyl sulfate (SDS) at 20 °C.

This plot can be used to estimate the CMC (critical micelle concentration).



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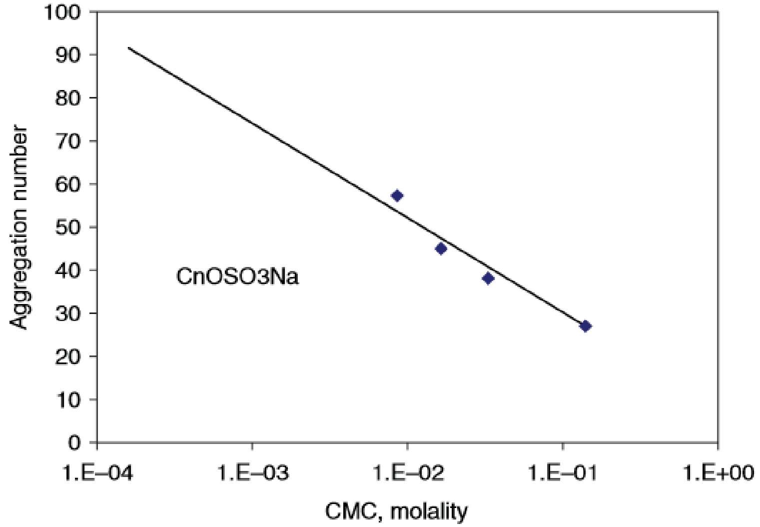
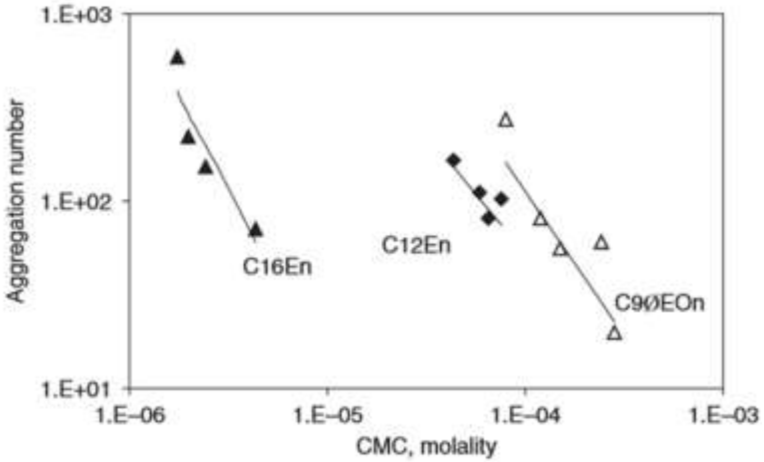
Aggregation number of ionic and non-ionic surfactants



The number of surfactants in a micelle is called the "aggregation number" (N_{agg}) and is about 50–100 for spherical micelles.

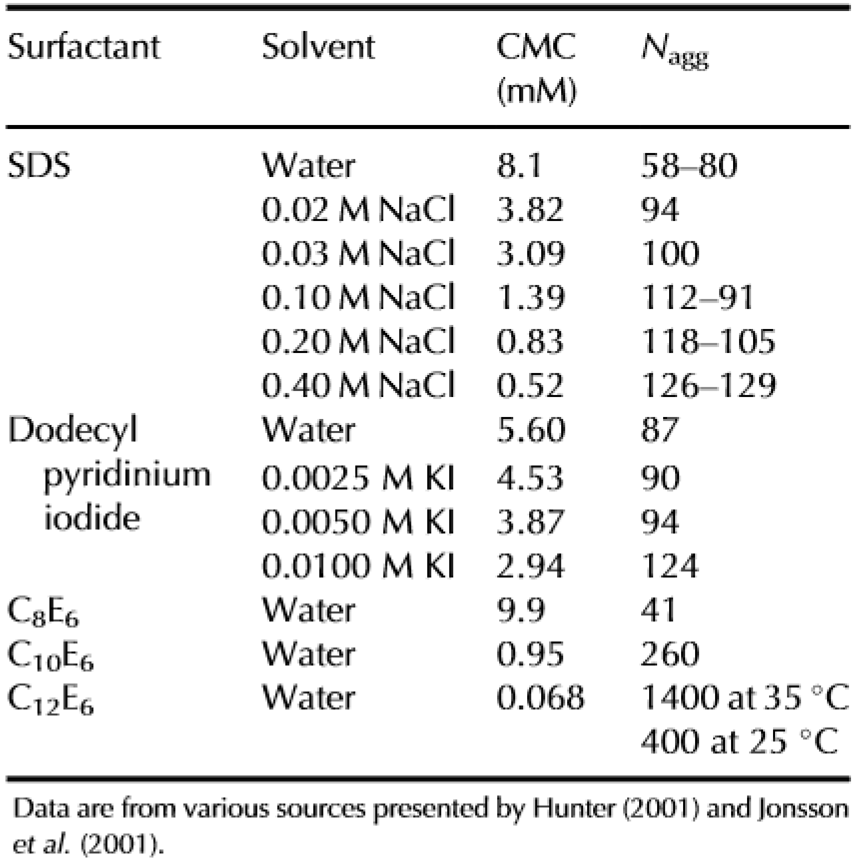
The aggregation number can be estimated from the ratio of the volume of the micelle to the volume of a surfactant molecule or, equivalently, as the surface area of a micelle divided by the surface area of the surfactant head:

$$N_{agg} = \frac{V_{micelle}}{V_{surfactant}} = \frac{A_{micelle}}{A_{surfactant}}$$



The aggregation number and CMC

The aggregation number increases with decreasing CMC and with increasing salt concentration, as shown for two surfactant families in Table.



Surfactant	Solvent	CMC (mM)	N_{agg}
SDS	Water	8.1	58–80
	0.02 M NaCl	3.82	94
	0.03 M NaCl	3.09	100
	0.10 M NaCl	1.39	112–91
	0.20 M NaCl	0.83	118–105
	0.40 M NaCl	0.52	126–129
Dodecyl pyridinium iodide	Water	5.60	87
	0.0025 M KI	4.53	90
	0.0050 M KI	3.87	94
	0.0100 M KI	2.94	124
C_8E_6	Water	9.9	41
$C_{10}E_6$	Water	0.95	260
$C_{12}E_6$	Water	0.068	1400 at 35 °C 400 at 25 °C

Data are from various sources presented by Hunter (2001) and Jonsson *et al.* (2001).

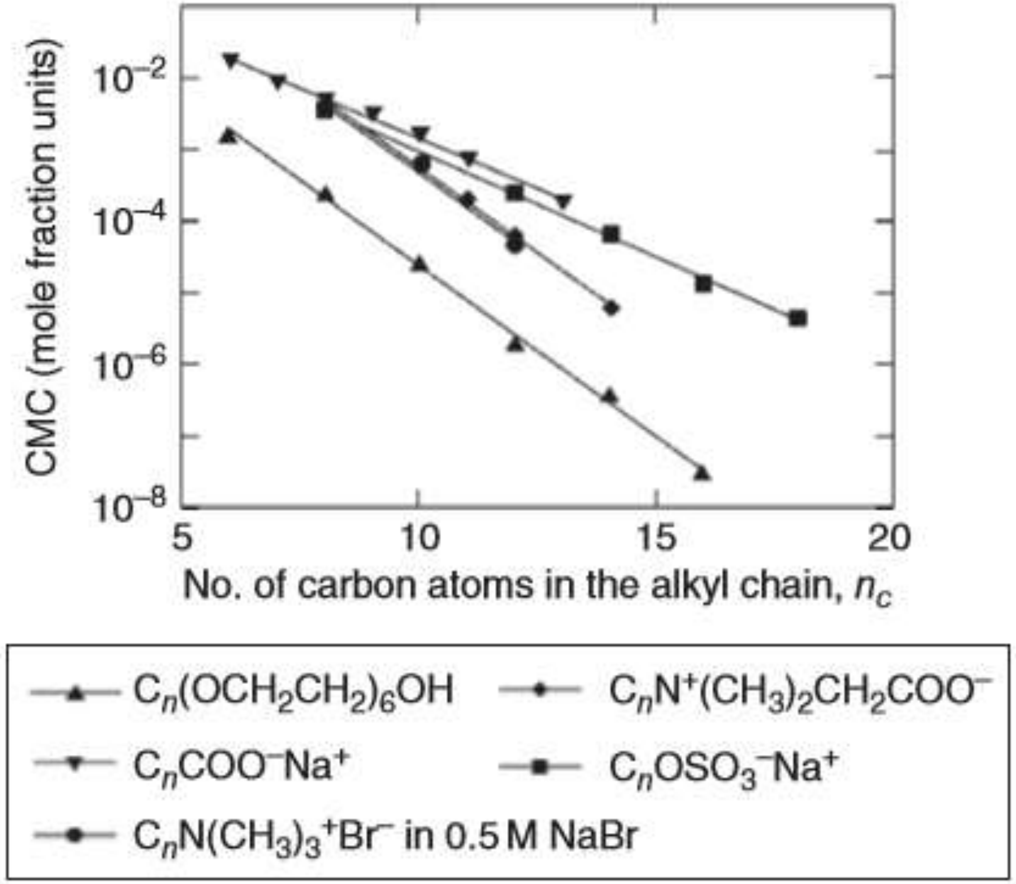
CMC salt concentration and chain length

For non-ionics, salts do not have an important influence.

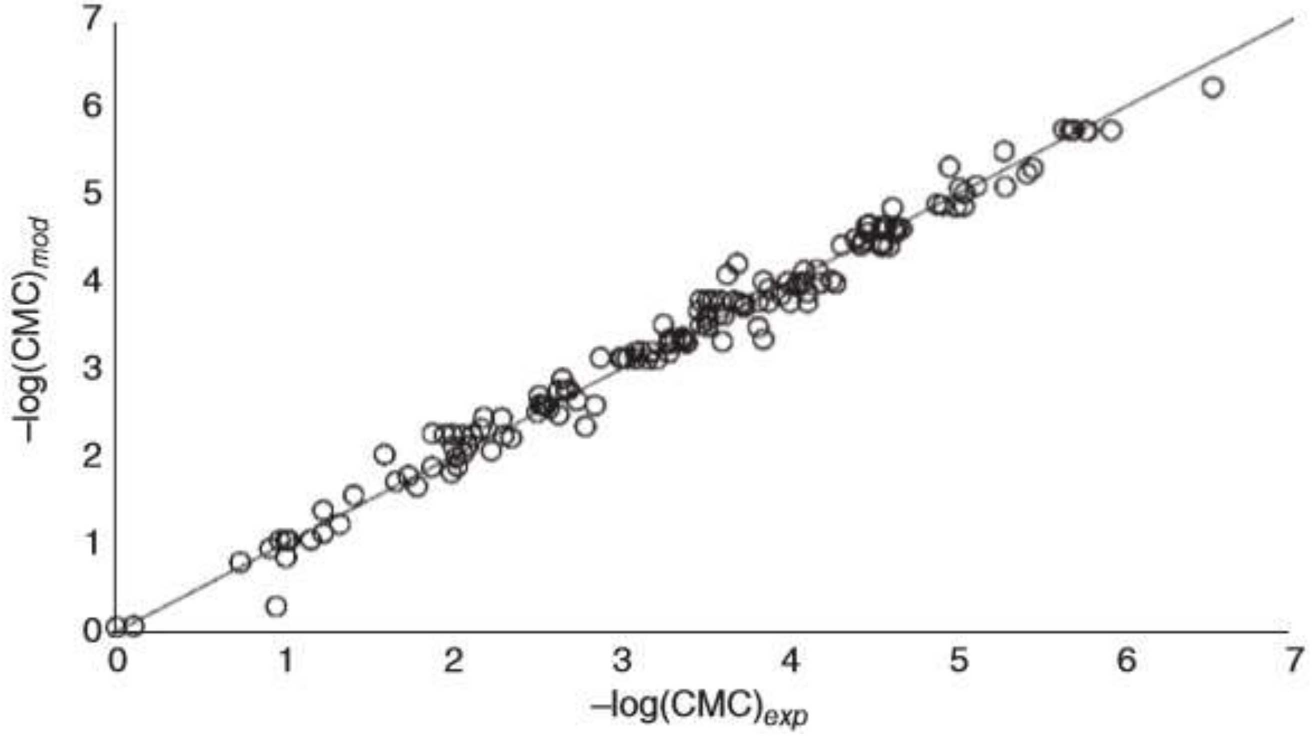
However, for ionic surfactants, salts result in a drastic decrease of CMC.

This is due to the reduction of the repulsions between the charged head groups of the surfactants.

The effect of chain length is more pronounced for the non-ionic surfactants. The decrease of CMC is pronounced until there are 18 carbon atoms in the chain, after which CMC tends to be rather constant, possibly due to coiling of the hydrophobic chains in the water phase.



Experimental versus predicted (via the group contribution method) values of CMC for a wide range of non-ionic surfactants

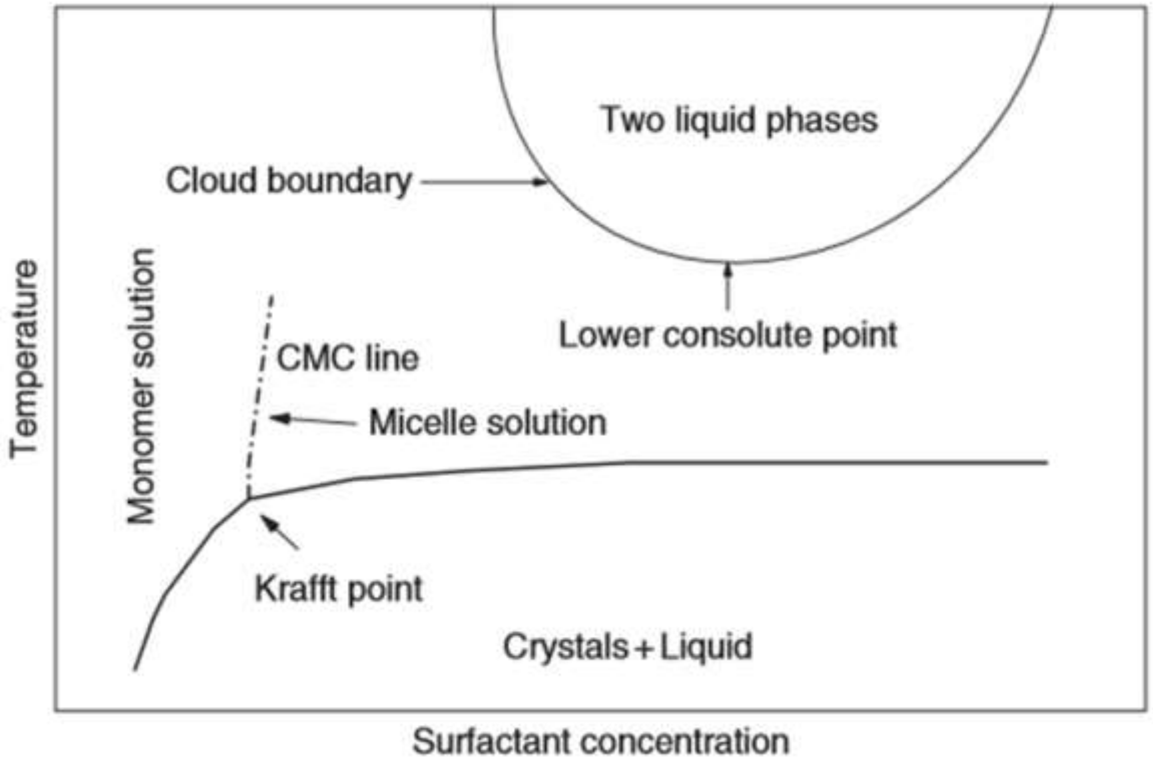


Micellization – theories and key parameters

Micelles only appear after a certain temperature is reached, the so-called "Krafft point".

In other words, the Krafft point is the temperature above which micelles are created.

The surfactant must be in fluid form and thus the Krafft temperature is essentially close to the melting point of the chain term of the ionic surfactant.



Krafft temperature and cloud point

In general, the longer the hydrocarbon chain length, the higher the Krafft temperature.

For this reason, shorter-chain-length surfactants or branched chain soaps are used for cold-water detergent formulations.

Non-ionic surfactants suffer the inverse problem and become insoluble with increasing temperature.

This is because their polar head groups become less hydrophilic with increasing temperature and a 'cloud point' is reached where they precipitate from solution.

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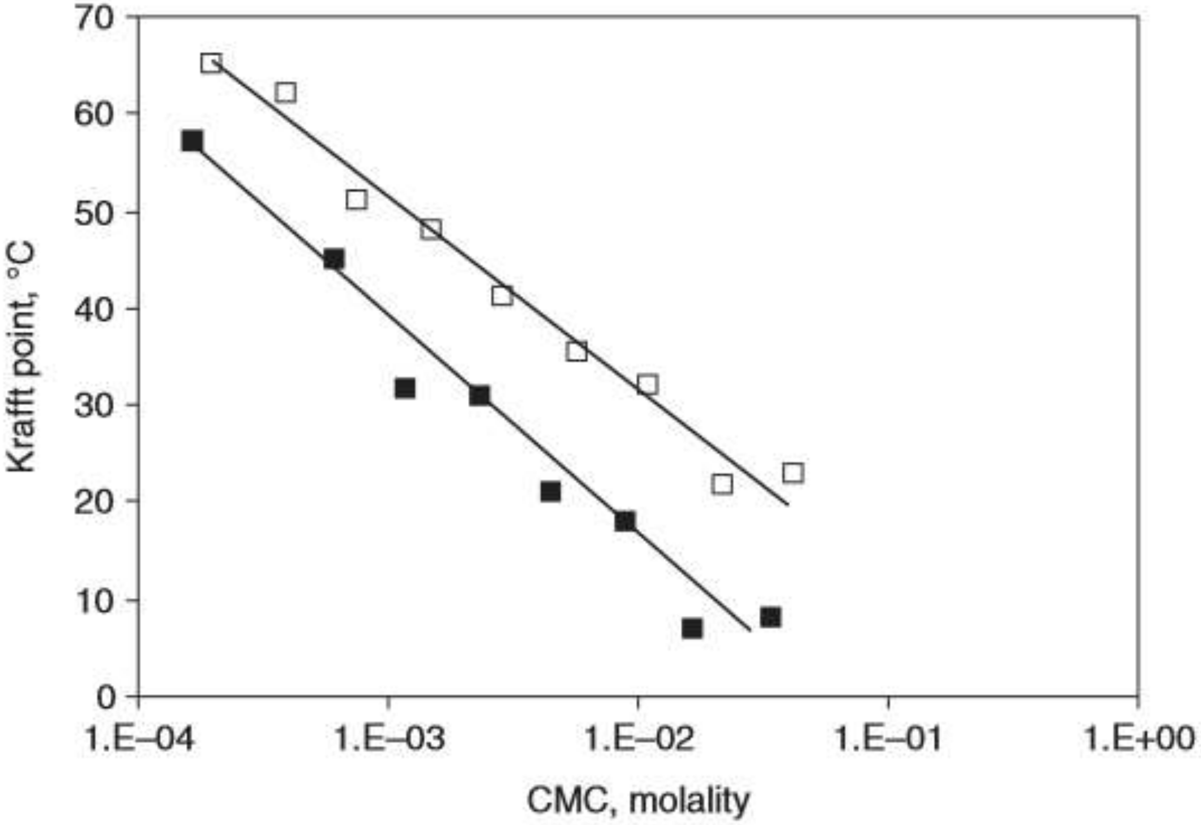
Krafft–CMC relationship for two families of surfactants (black: sodium alkyl sulfates, white: sodium alkyl sulfonates)

Low Krafft temperatures are linked to surfactants having high CMC, i.e. low chain lengths.

This is because, long-chain ionic surfactants create micelles at low concentrations, but this happens at rather high temperatures.

A length of the hydrophobic chain of about 12–14 or 16 atoms is often a good compromise.



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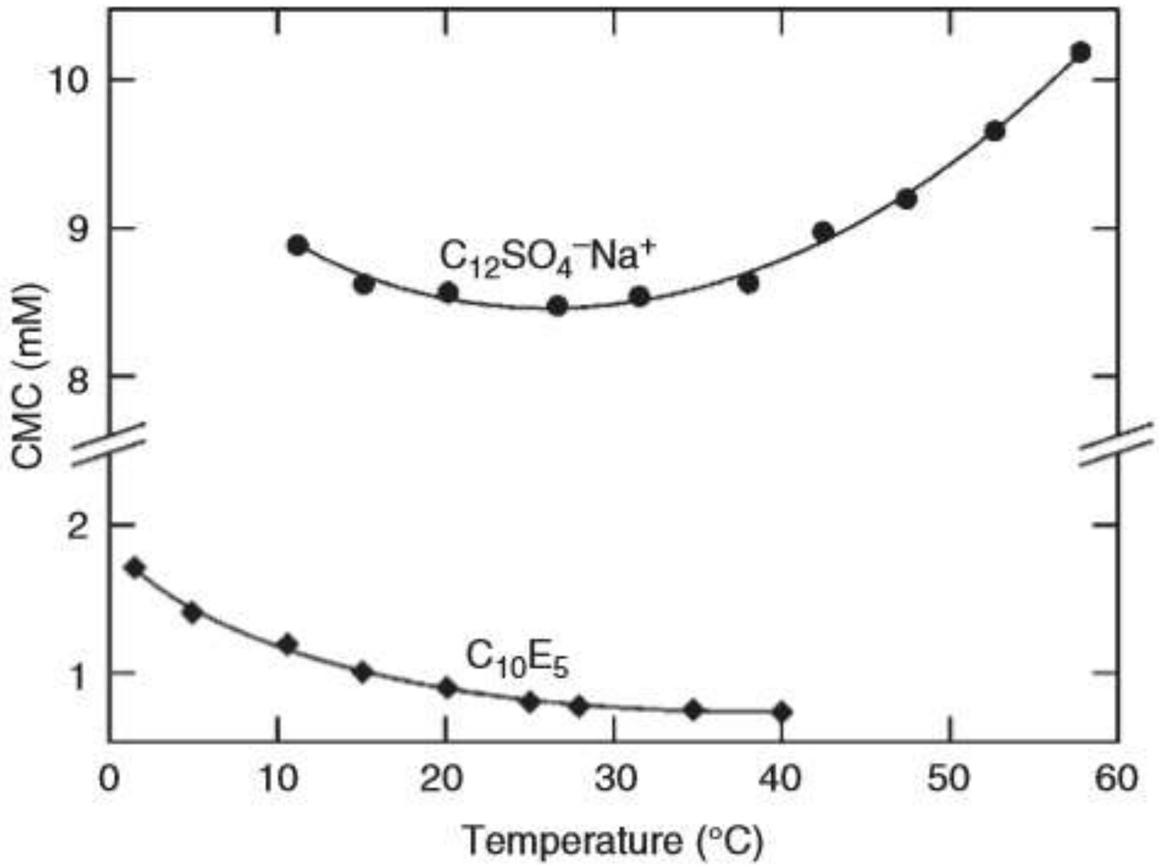
The temperature dependency of CMC is rather complex

CMC does not depend very much on temperature (due to a balance between enthalpic and entropic effects).

CMC increases with increasing temperature for ionic surfactants because micellization is an exothermic process, but there are exceptions.

SDS (sodium dodecyl sulfate) presents a minimum in the CMC–temperature plot and, thus, at low temperatures the micellization must be endothermic.

CMC decreases with increasing temperature for non-ionic surfactants, e.g. the polyoxyethylenes.



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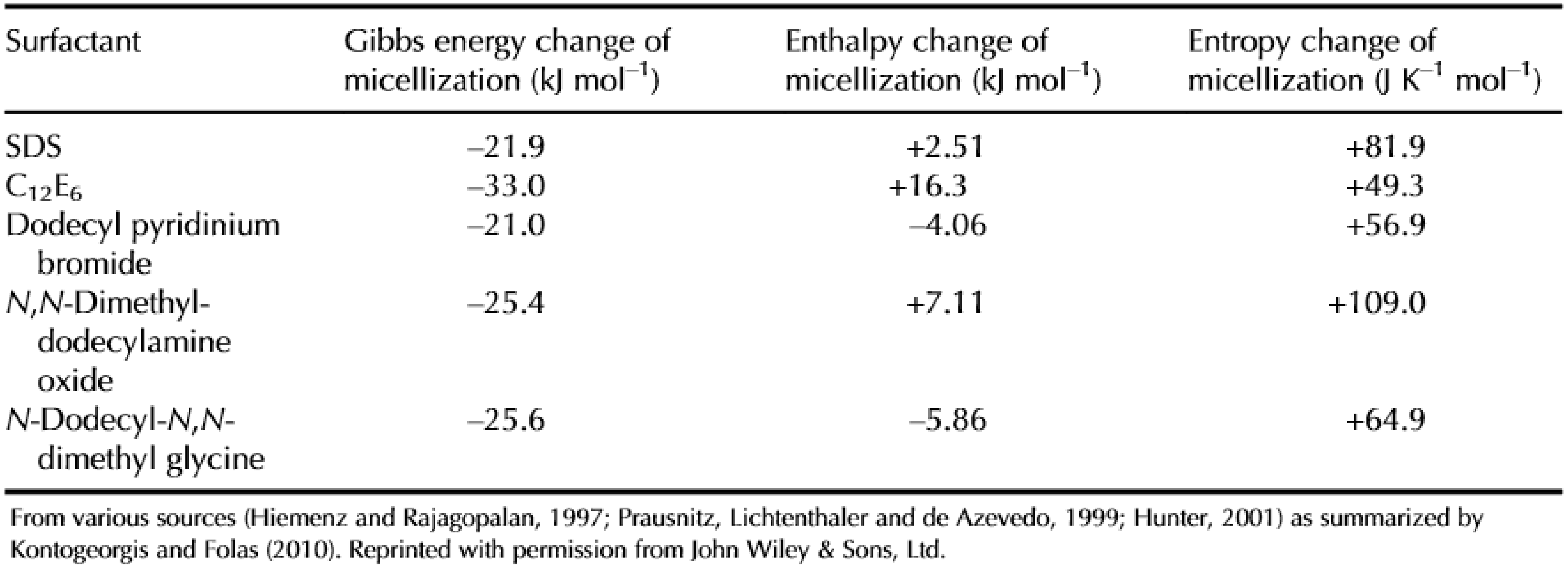
Enthalpy, entropy and Gibbs free energy change during the micellization process



Surfactant	Gibbs energy change of micellization (kJ mol^{-1})	Enthalpy change of micellization (kJ mol^{-1})	Entropy change of micellization (J K^{-1} mol^{-1})
SDS	–21.9	+2.51	+81.9
$C_{12}E_6$	–33.0	+16.3	+49.3
Dodecyl pyridinium bromide	–21.0	–4.06	+56.9
N,*N*-Dimethyl-dodecylamine oxide	–25.4	+7.11	+109.0
N-Dodecyl-*N*,*N*-dimethyl glycine	–25.6	–5.86	+64.9

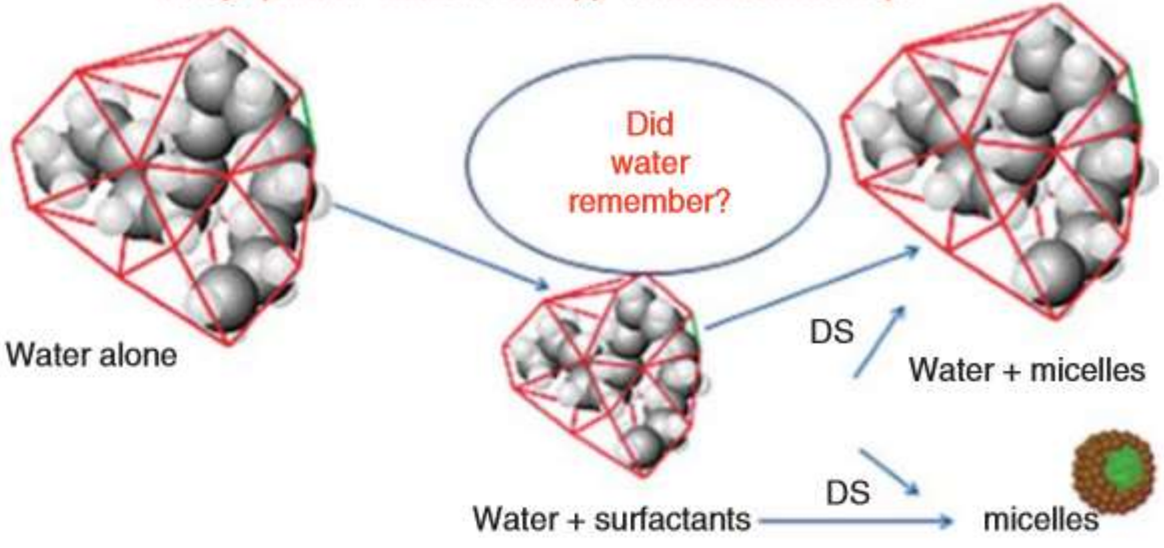
From various sources (Hiemenz and Rajagopalan, 1997; Prausnitz, Lichtenthaler and de Azevedo, 1999; Hunter, 2001) as summarized by Kontogeorgis and Folas (2010). Reprinted with permission from John Wiley & Sons, Ltd.

It is an entropic phenomenon with high positive values of the entropy change, which are typically attributed to the changes of the structure of water in the presence of surfactants and micelles, i.e. the so-called hydrophobic effect

The micellization process in surfactant solutions is an entropic effect.

Water molecules due to their very strong tendency to be with each other ("and far away from the hydrophobic enemies") create (in the presence of hydrophobic compounds) a higher degree of local order than in pure liquid water (entropy decrease).

Micellization is (almost always) an entropic effect, i.e. the driving force behind aggregation of surfactant molecules is a large positive value of entropy of micellization! why?

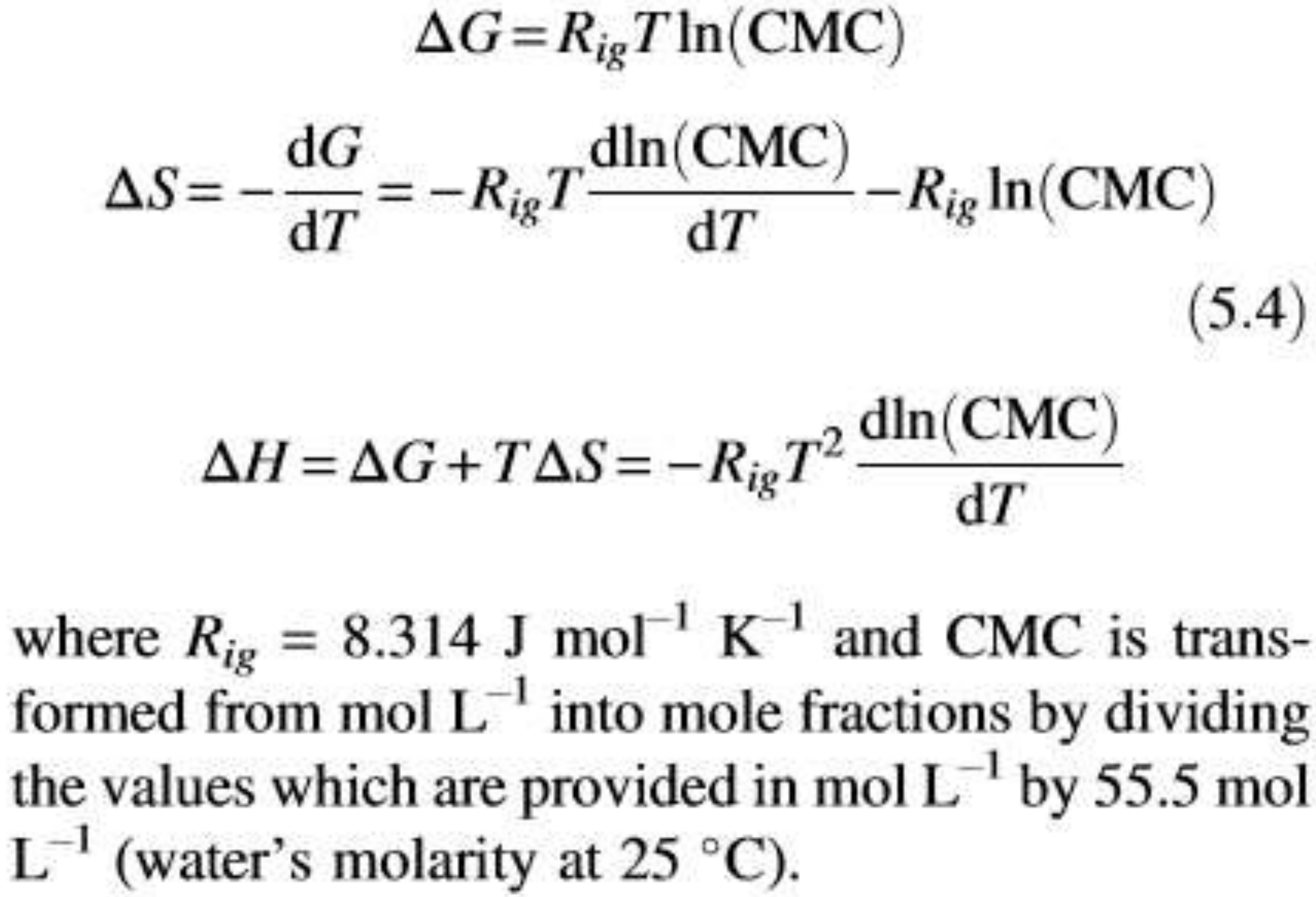


The protagonist is WATER!!

The energy and entropy changes during the micellization

Assuming that the enthalpy of micellization is almost constant within a certain temperature range, then the quantity ln(CMC) can be seen to be linear with respect to 1/T.

The enthalpy of micellization could be obtained from the slope of such a plot.



$$\Delta G = R_{ig} T \ln(\mathrm{CMC})$$

$$\Delta S = -\frac{\mathrm{d}G}{\mathrm{d}T} = -R_{ig} T \frac{\mathrm{d}\ln(\mathrm{CMC})}{\mathrm{d}T} - R_{ig} \ln(\mathrm{CMC}) \quad (5.4)$$

$$\Delta H = \Delta G + T\Delta S = -R_{ig} T^2 \frac{\mathrm{d}\ln(\mathrm{CMC})}{\mathrm{d}T}$$

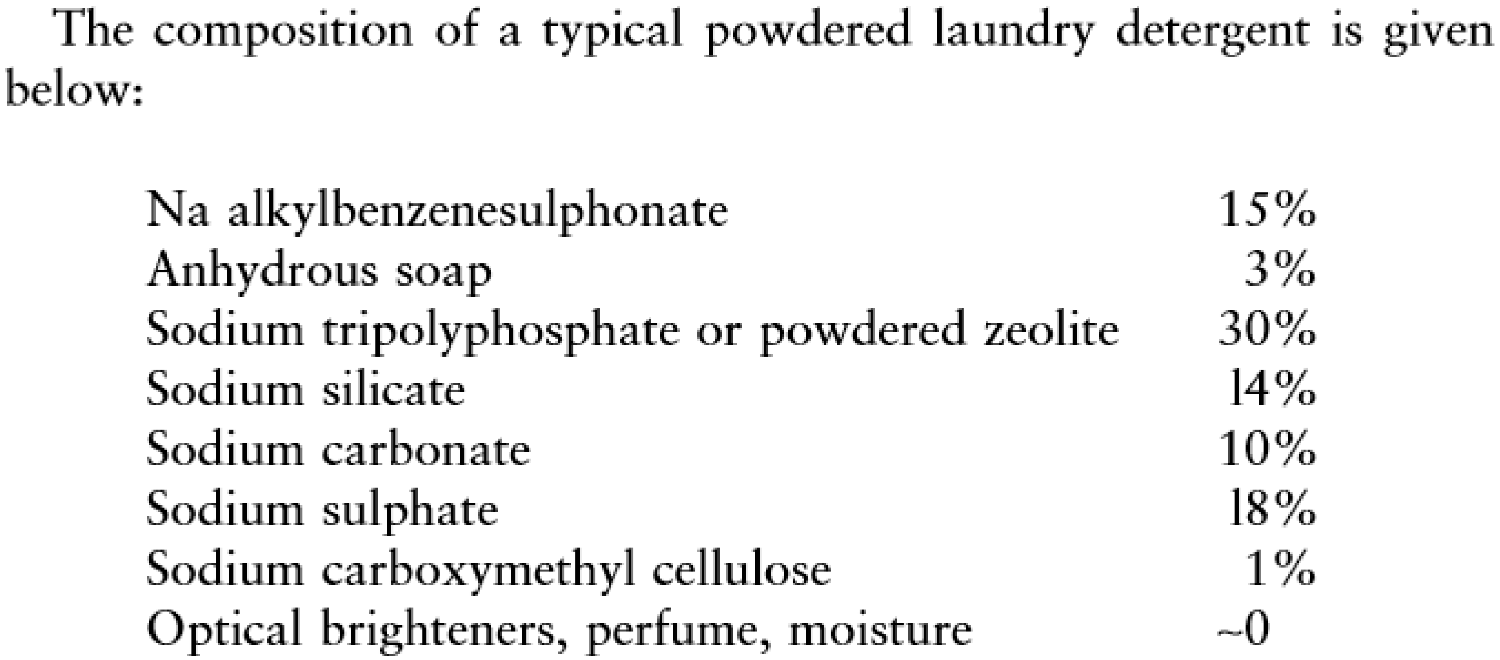
where $R_{ig} = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and CMC is transformed from mol $\mathrm{L^{-1}}$ into mole fractions by dividing the values which are provided in mol $\mathrm{L^{-1}}$ by 55.5 mol $\mathrm{L^{-1}}$ (water's molarity at 25 °C).

Surfactants and cleaning (detergency)

A detergent is a very complex chemical product.

Its cleaning ability depends on several factors: type of surfactant and other compounds (chemistry), the concentration of contaminants, the mechanical energy used, the time, the temperature, the type of surface, etc.

In the detergency process, fatty materials (i.e. dirt, often from human skin) are removed from surfaces, such as cloth fibres, and dispersed in water.



The composition of a typical powdered laundry detergent is given below:

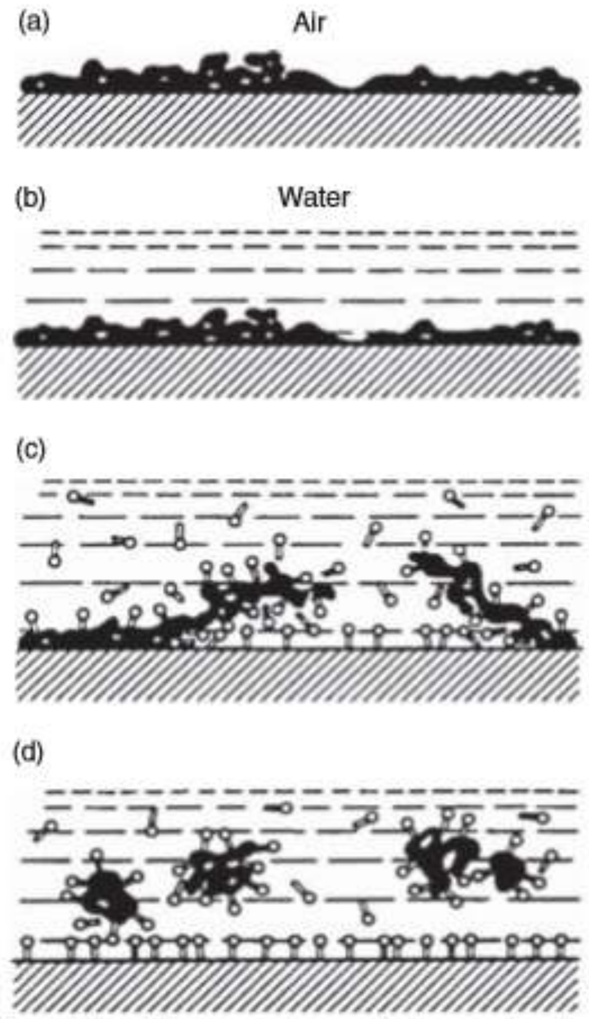
Na alkylbenzenesulphonate	15%
Anhydrous soap	3%
Sodium tripolyphosphate or powdered zeolite	30%
Sodium silicate	14%
Sodium carbonate	10%
Sodium sulphate	18%
Sodium carboxymethyl cellulose	1%
Optical brighteners, perfume, moisture	~0

The creation of a foam is not necessary for detergent action in a conventional washing machine.

How do we clean the various surfaces?

We can roughly summarize the major mechanisms of surfactant cleaning in the following three steps:

- improving the wetting of surfaces by decreasing the surface tension of water/aqueous solution (water alone cannot in most cases provide good wetting);
- good adhesion on substrate and dirt and reduction of the interfacial tensions between dirt(d) water(w) and solid substrate(s)-water and thus reducing the corresponding work of adhesion, since the interfacial tensions between dirt–water and solid–water are reduced ($W_{adh,ds} = \gamma_{sw} + \gamma_{dw} - \gamma_{sd}$);
- solubilization of dirt inside micelles, which ensures that the dirt is removed with little mechanical help, thus avoiding deposition of the dirt back on the surface



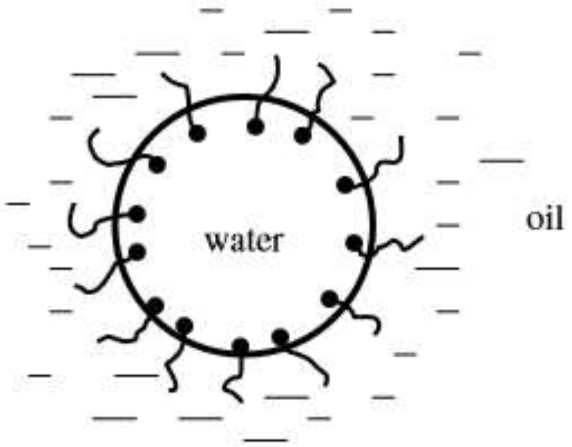
Dry-cleaning

An inverted type of detergency process is used in dry-cleaning.

Usually tetrachloroethylene is used to dissolve grease from materials that should not be exposed to water.

However, because complete cleaning must also remove polar materials which are insoluble in C_2Cl_4, surfactants and a small amount of water are added, forming inverted micelles.

Polar materials are then solubilized inside the aqueous core of the micelle and the material is not exposed to water, even though the process is not entirely dry.



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Important parameters of detergency

The properties (e.g. cleaning and stabilizing capabilities) of surfactants depend on both solution properties (temperature, time, presence of salts and co-surfactants) and the characteristics of the surfactants, especially CMC, the Krafft point and their chemistry.

The surfactant chemistry and especially the balance between hydrophobic and hydrophilic parts are quantified using tools like the CPP or HLB (critical packing parameter, hydrophilic–lipophilic balance).

Important parameters affecting the performance of detergents are pH, presence of additives, nature of contaminants, type of surface, time/temperature and the mechanical energy used.

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Other applications of surfactants

Besides their use in detergents and in dispersions as stabilizers, surfactants find many more applications. One interesting application is their solubilization capability inside micelles.

For example, the dye xylenol orange (a colourant) dissolves sparingly in pure water but gives a deep red solution with SDS at concentrations above CMC. This method can be used experimentally for determining (measuring) the CMC.

Hydrocarbons and non-polar compounds solubilize inside the micelle, while fatty acids and alcohols solubilize in the area close to the heads of the surfactants of the micelle

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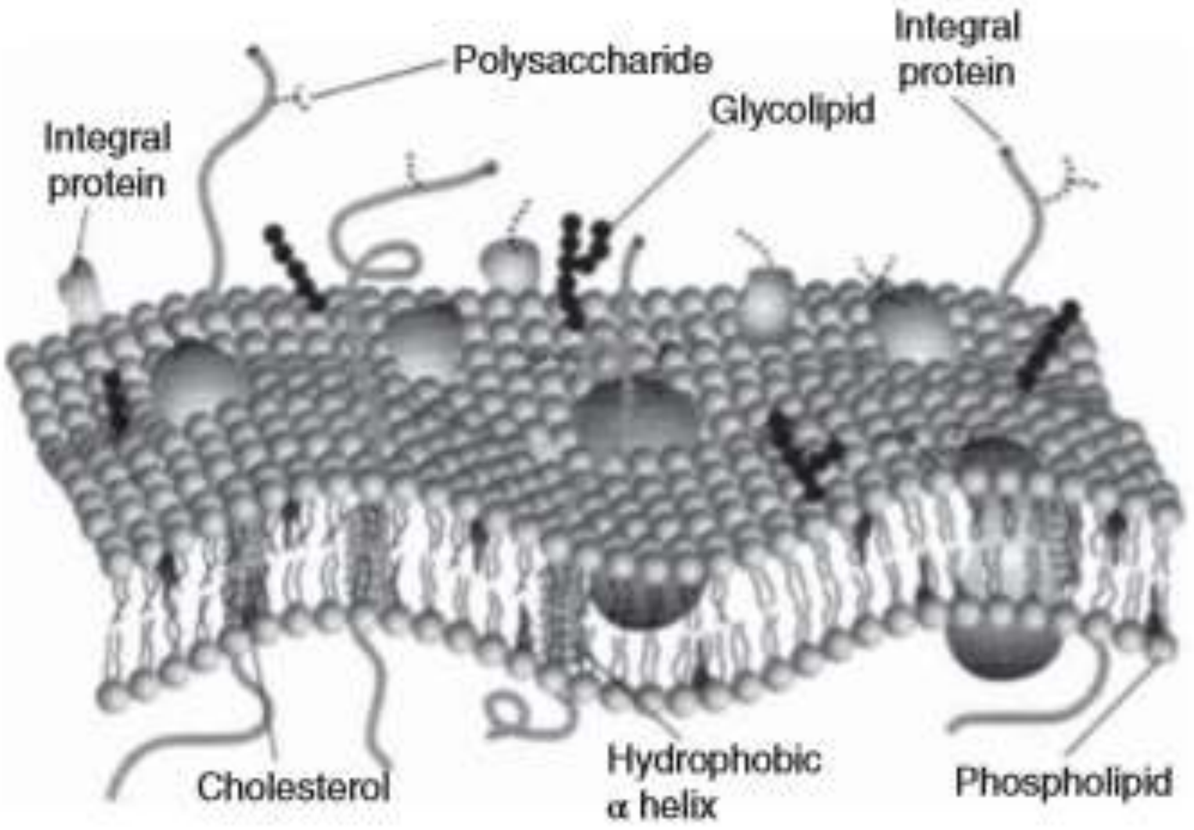
Other applications of surfactants

Reverse micelles can be used as mini-reactors for enzyme-catalysed reactions.

These reactions require an aqueous environment but often the reactants are only sparingly soluble in water.

Surfactants play a crucial role in the study of many biological systems, e.g. biological membranes



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Author, Editor and Referee References

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Refereeing of this material was done by: ____________________

Editing into NETCHEM Format and onto NETCHEM platform was completed by: Milan Milosevic, Tatjana Andjelkovic

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References and Supplemental Material

The NETCHEM platform was established at the University of Nis in 2016-2019 through the Erasmus Programme.

Please contact a NETCHEM representatives at your institution or visit our website for an expanded contact list.

The work included had been led by the NETCHEM staff at your institution.

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Adsorption in Colloid and Surface Science

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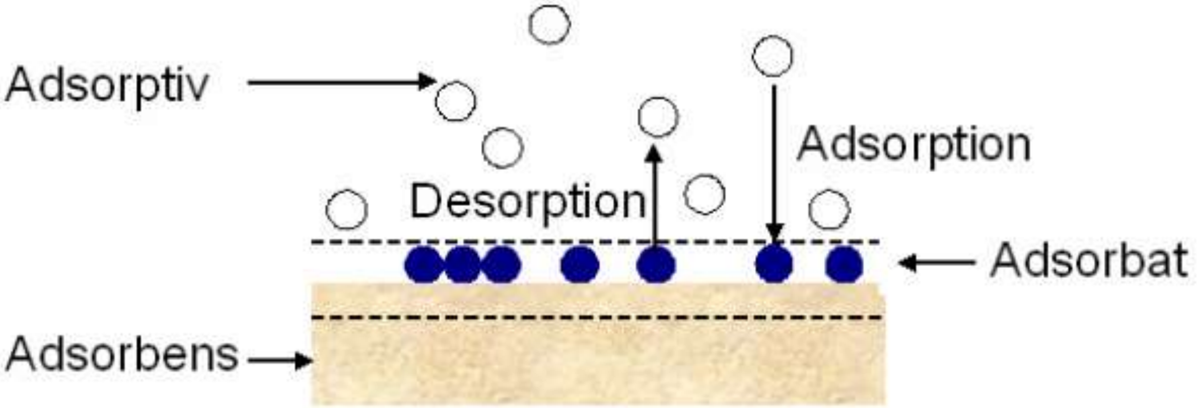
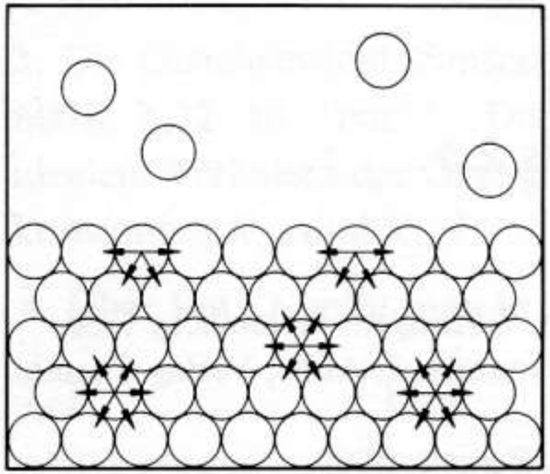
Terms and definitions

A foreign material in gaseous or liquid form (the adsorptive) becomes attached to a solid or liquid surface, the adsorbent, and forms the adsorbate.

In the surface region, the interaction forces responsible for the bulk properties change, they become asymmetric, since the outermost bonds are unsaturated, resulting in a peculiar chemical reactivity of the surface.

In our context the most important consequence is that the surface becomes capable of adsorbing foreign atoms or molecules.





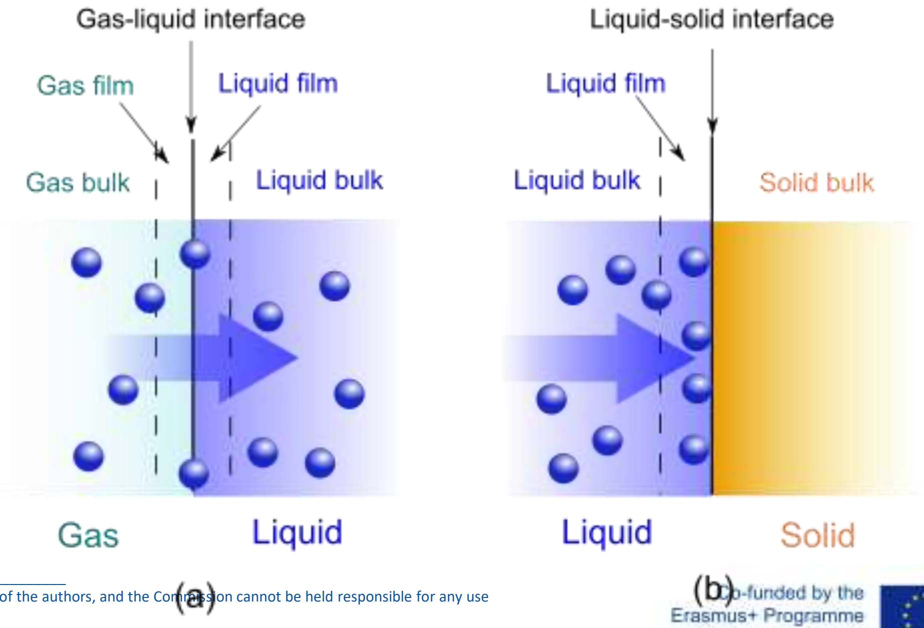
Universality of adsorption - overview

High surface areas exist in porous materials: activated carbon, alumina or silica gel. These materials have "huge" surface areas (per g).

Important parameters of the solid surface:

- the form,
- specific surface area,
- porosity,
- polarity,
- surface energy and chemical homogeneity, including the number of adsorption sites.

Adsorption versus Absorption



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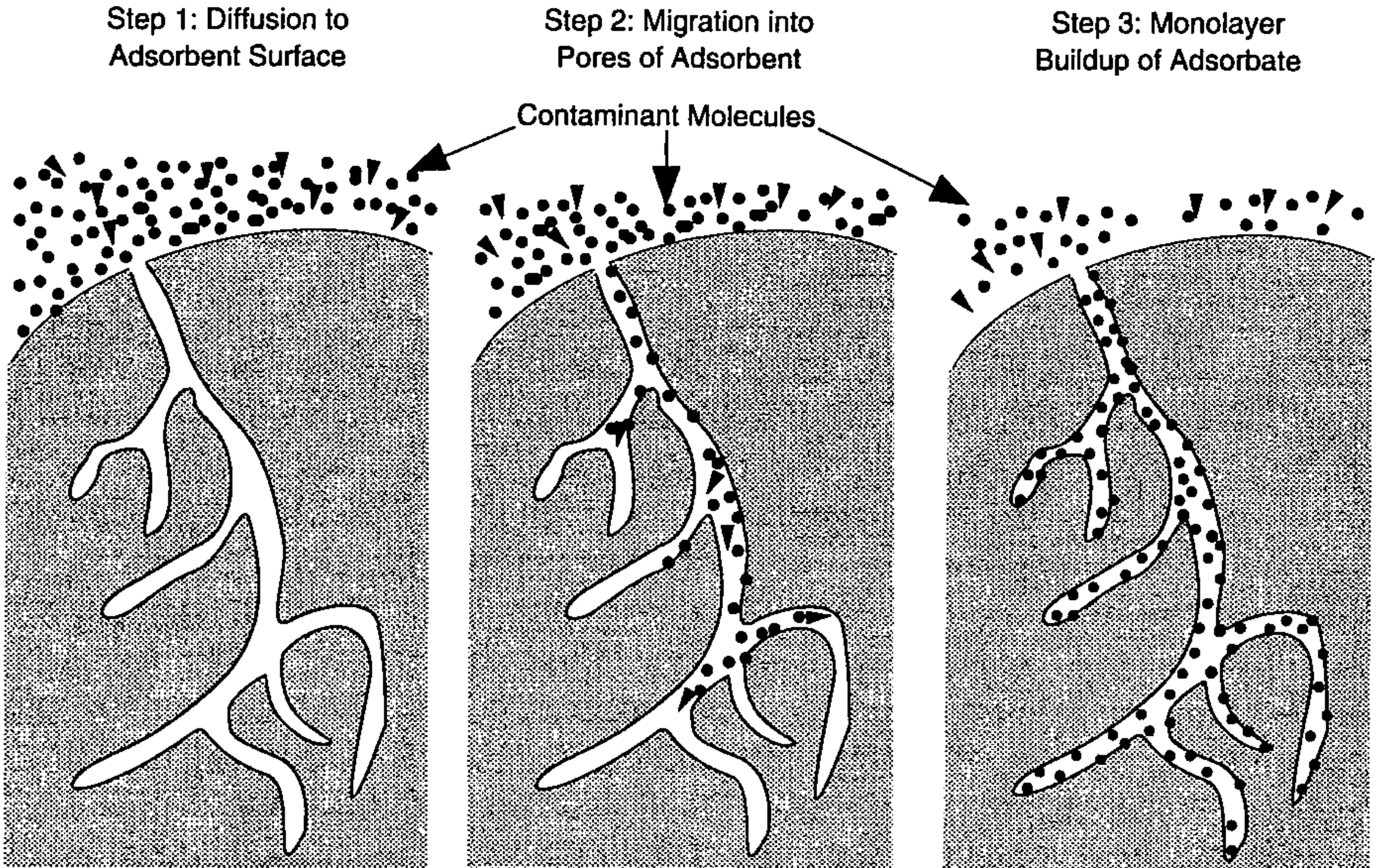
Adsorption onto porous solids



Application

There are numerous applications of adsorption:

- **stabilization,**
- **cleaning,**
- **heterogeneous catalysis including catalytic converters in cars,**
- **separations like drying,**
- **surface modification and change of properties like foaming or rheological ones,**
- **measurement of the surface area of powders and other solid surfaces,**
- **for selective separations (like removing pollutants).**

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Adsorption theories

The quality of the fit to the data is important but cannot serve alone as a criterion for selecting the best theory.

This is because the ability of an equation to fit the shape of an experimental isotherm does not provide a sensitive test for the model on which the equation was based.

Comparison between direct (calorimetric) experimental data of the heat of adsorption and the values obtained by the adsorption theory can provide a much more rigorous test for checking the theories.

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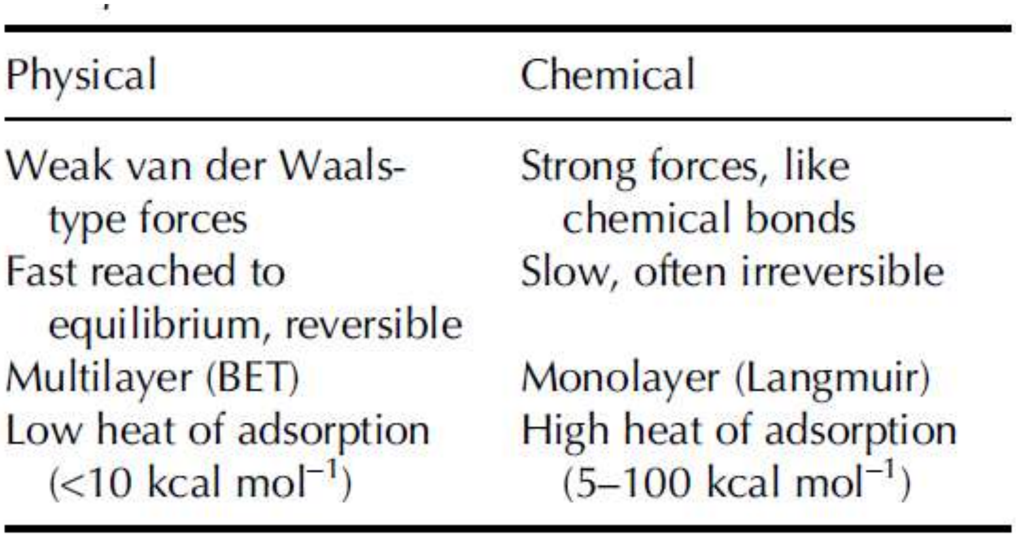
Adsorption of gases on solids

The adsorption of gases on solids can be either of physical or chemical nature.

The physical multilayer adsorption is often faster than the chemical adsorption but with a low heat of adsorption, <10 kcal mol^{-1} versus 5–100 kcal mol^{-1} for the chemical one.



Physical	Chemical
Weak van der Waals-type forces	Strong forces, like chemical bonds
Fast reached to equilibrium, reversible	Slow, often irreversible
Multilayer (BET)	Monolayer (Langmuir)
Low heat of adsorption (<10 kcal mol^{-1})	High heat of adsorption (5–100 kcal mol^{-1})

Langmuir model

The Langmuir theory is derived based on many simplifying assumptions:

- “ideal” (clean, smooth, homogeneous, nonporous) surface;
- existence of active centres on the surface; Each centre (site) can be free or occupied by an adsorbed molecule;
- only one molecule per active centre;
- no interactions between adsorbed molecules, i.e. homogeneous surface;
- all sites are equivalent (same heat of adsorption);
- no solute–solvent interactions;
- solute and solvent have same size;
- dilute solutions;
- monolayer coverage.

Langmuir model

The Langmuir theory has been derived based on the assumption that the adsorption rate is proportional to the concentration in the solution and the fraction of free non-covered area of the adsorbent.

The desorption rate, on the other hand, is assumed to be proportional to the fraction of surface covered by adsorbate molecules.

At equilibrium, the adsorption and desorption rates are equal.

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Langmuir model

All these assumptions do not restrict aplicability of Langmuir model in chemical adsorption and physical adsorption at low pressures and a high temperatures.

It can fit a plateau shaped curve, which many monolayers and in general many adsorption phenomena follow.

The mathematical representation of the Langmuir equation is:

$$\Theta = \frac{V}{V_m} = \frac{B.P}{1+B.P} \Rightarrow \frac{P}{V} = \frac{P}{V_m} + \frac{1}{B.V_m}$$

Θ is the fraction of occupied active centres. The volume *V* is expressed in, for example, $cm^3\,g^{-1}$ (solid). *P* is the pressure, while V_m and *B* are adjustable parameters, respectively, the volume of the monolayer and the affinity parameter. The higher the *B*-parameter is, the higher is the affinity of a gas for the solid.

Langmuir model

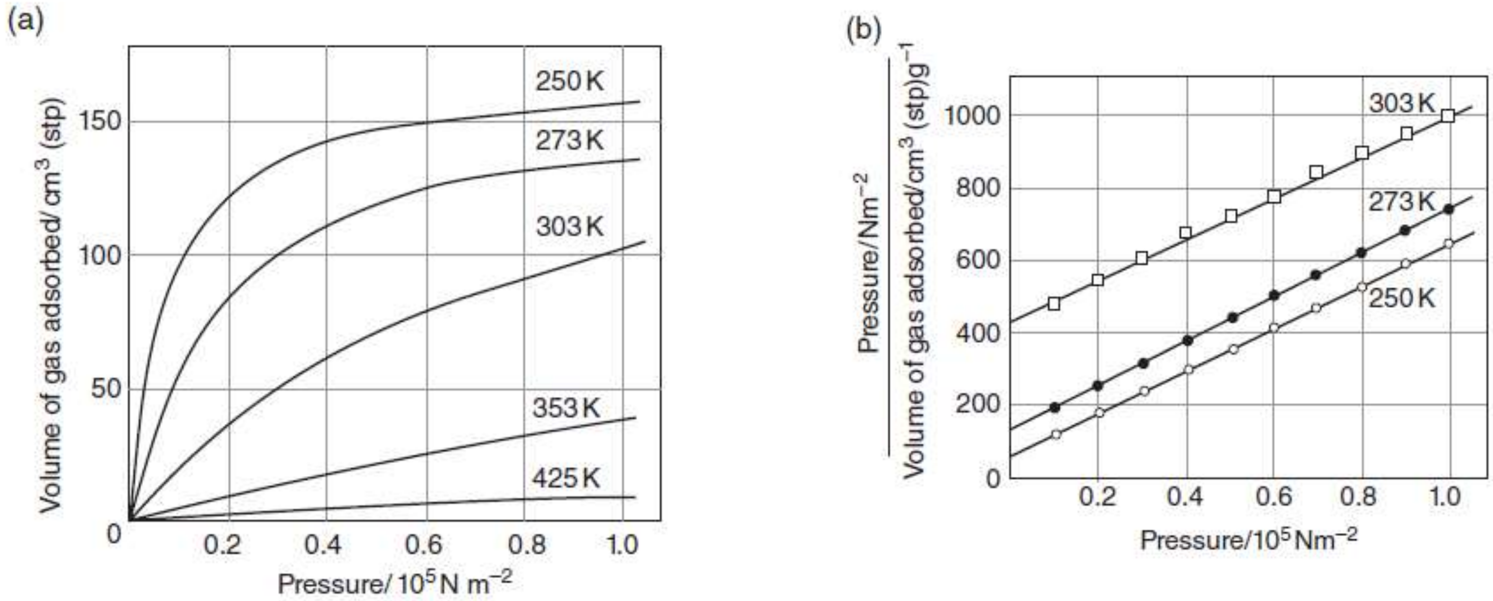
The Langmuir equation can be derived both thermodynamically and kinetically;

The latter derivation is simple and assumes that the rate of adsorption is equal to the rate of desorption.

Adsorption of gases is an exothermic process (with a negative entropy of adsorption) as the molecules are confined in two dimensions.

Direct (calorimetric) experimental data of the heat of adsorption are very useful for checking adsorption theories

Typical Langmuir adsorption



Adsorption isotherms for ammonia on charcoal: (a) as plots of the volume of gas (per mass of solid), V, as a function of pressure (P) at constant temperature (T) and (b) in linearized Langmuir plots. Shaw(1992). Reproduced with permission from Elsevier

Adsorption of gases on solids using the BET equation

Stephen Brunauer (1903–1986), Paul Emmett and Edward Teller (1908–2003) developed a theoretically based multilayer adsorption theory.

Like the Langmuir equation, it is also a two-parameter adsorption isotherm.

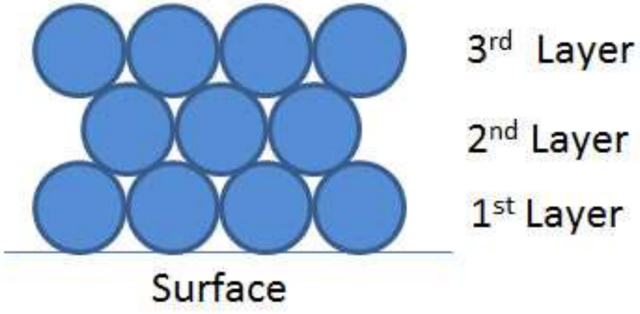
The parameter C of BET is a measure of the difference in the heat of adsorption of the 2nd, 3rd and so on layer compared to the heat of the creation of the first layer.

The results are not always in excellent agreement with calorimetric measurements.

$$\frac{P}{V(P_o-P)}=\frac{1}{CV_m}+\frac{C-1}{CV_m}\frac{P}{P_o}$$

Langmuir model

Brunauer Emmett Teller (BET) model



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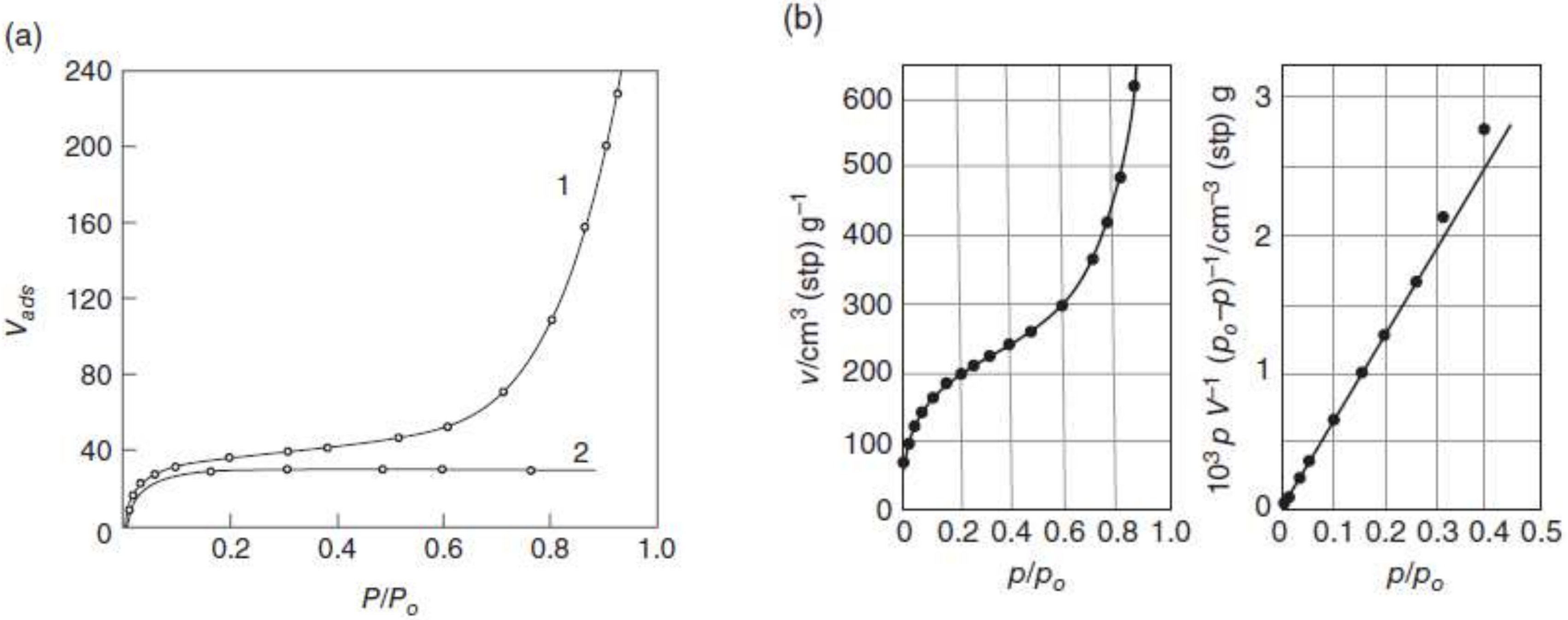
Comparison of Langmuir and BET adsorption



(a) Comparison of two adsorptions: that of nitrogen on silica is a physical BET adsorption at 77 K (curve 1), while oxygen's adsorption on charcoal at 150 K (curve 2) is a chemical Langmuir adsorption. Notice that the y-axis is the pressure divided by the saturation pressure. (b) Adsorption isotherm for nitrogen on silica gel in the linearized form of the BET equation. From Shaw (1992)

BET equation

The two parameters can be obtained from a specific linear plot:

$$\frac{P}{V(P_o - P)} = \frac{1}{CV_m} + \frac{C-1}{CV_m}\frac{P}{P_o}$$

V_m is simply calculated as 1/(slope + intercept)

With the exception of the first layer, all other layers are assumed to have the same heat of adsorption.

The model has been used for the characterization of porous materials, i.e. getting information about the surface area and the nature of the surface.

$$A_{spec} = \frac{V_m N_A}{V_g} A_o$$

$Vg = 22.414$ L mol^{-1}
A_o is the area occupied by one gas molecule (0.162 nm^2 for the often used N_2 at 77 K)

The BET theory has also its limitations

Absence of lateral interactions between adsorbed molecules;

Valid up to relative pressures (P/P_o) of 0.4;

Not always good agreement with calorimetric measurements;

Extension to n-layer for porous materials yield complex equations that cannot be expressed in linear form.

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Improvements of BET theory

Most improvements destroy the simplicity of the BET equation and the ease with which the experimental data can be analysed in a linear form to give values for the model's two parameters.

For these reasons, BET is typically used in its well-known form.

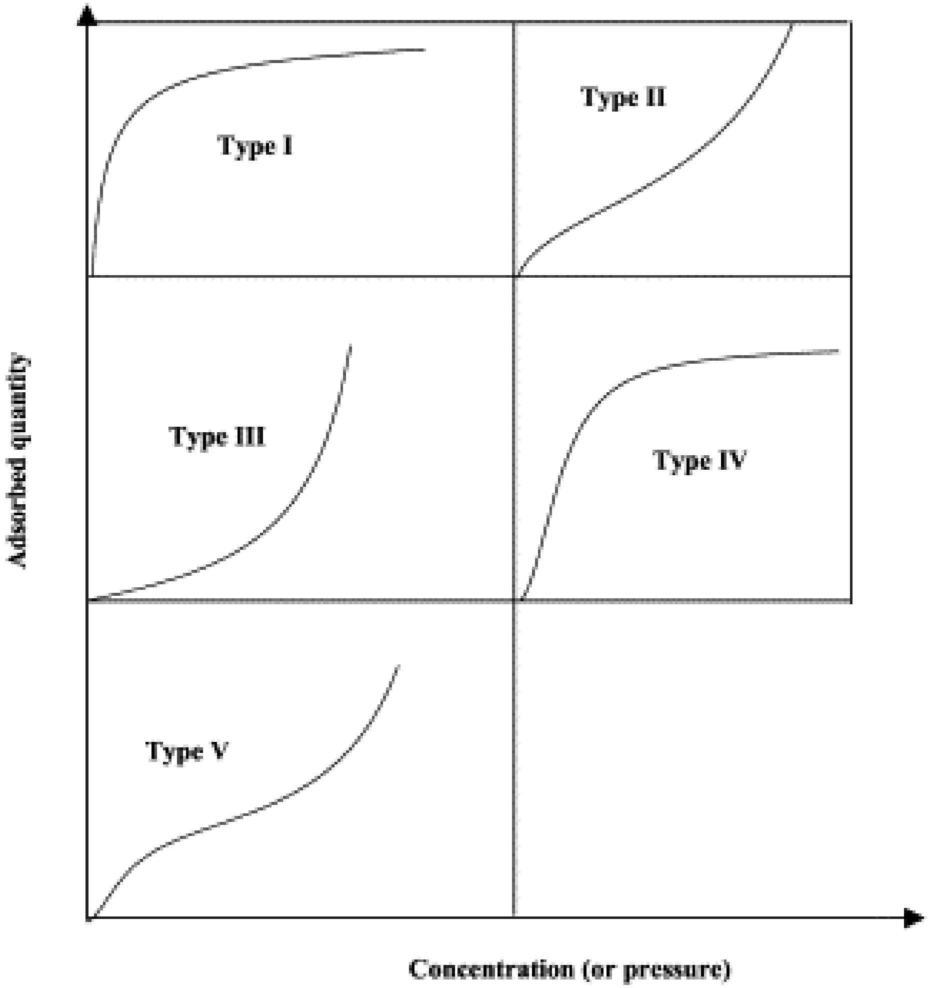
Brunauer classification

Type I is the monolayer chemical Langmuir-type adsorption.

Type II is the multilayer physical BET adsorption isotherm.

Type III is for – rather rarely occurring – weak adsorptions and

Types IV and V are for capillary condensation.

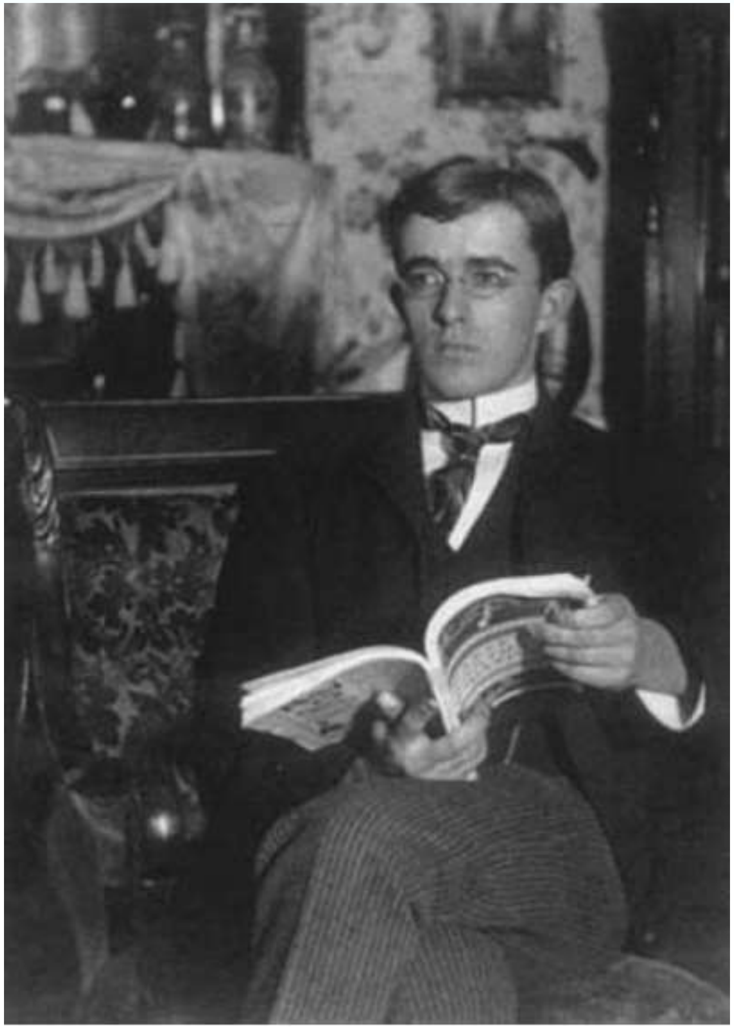


Adsorption from solution

The competition of solute and solvent for sites on the solid surface are very important.

The Langmuir theory is a very useful tool also for describing the adsorption of various compounds from solutions.

The two parameters of the Langmuir equation can be obtained in practice from experimental data using its linear form.



Langmuir equation

- Original and linear Langmuir form are:

$$q_e = \frac{q_m C_e}{1 + K_L C_e}$$

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}}$$

- Typical C_e and q_e units are respectively mol L^{-1} and mol g^{-1}, while A_{spec} is given in $m^2\ g^{-1}$. If A_{spec} and q_m are known then the area occupied by a molecule (A_0) can be calculated. *K* is a measure of the affinity of the solute for the surface

$$A_{spec} = q_m N_A A_0$$

- The parameter q_m is the adsorption at full coverage.

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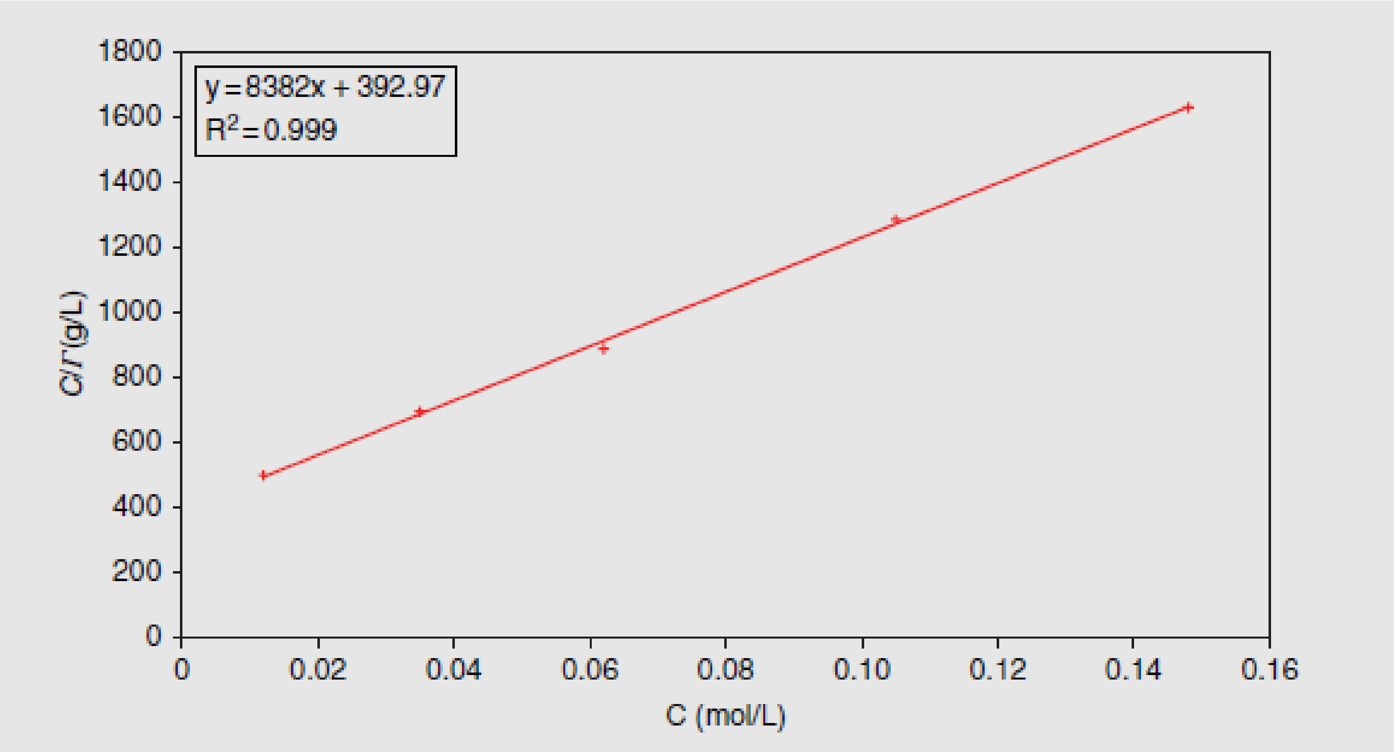
Gibbs energy and Langmuir equation

From the value of the solute–surface affinity parameter K in the Langmuir adsorption equation, it is possible to determine the Gibbs energy of adsorption:

$$\Delta G_{ads} = -R_{ig} T \ln k$$

The inverse of k (=1/k) is the concentration at which one half of the surface is occupied by the solute.

The adsorption of dodecanol (from solution in toluene) onto a sample of carbon black



Role of solvent

The adsorption of stearic acid on carbon black reaches different limiting values in different solvents; ranging from 10 mmol kg^{-1} when benzene is the solvent up to more than 40 mmol kg^{-1} when cyclohexane is the solvent.

The competition of solute and solvent for sites on the solid surface.

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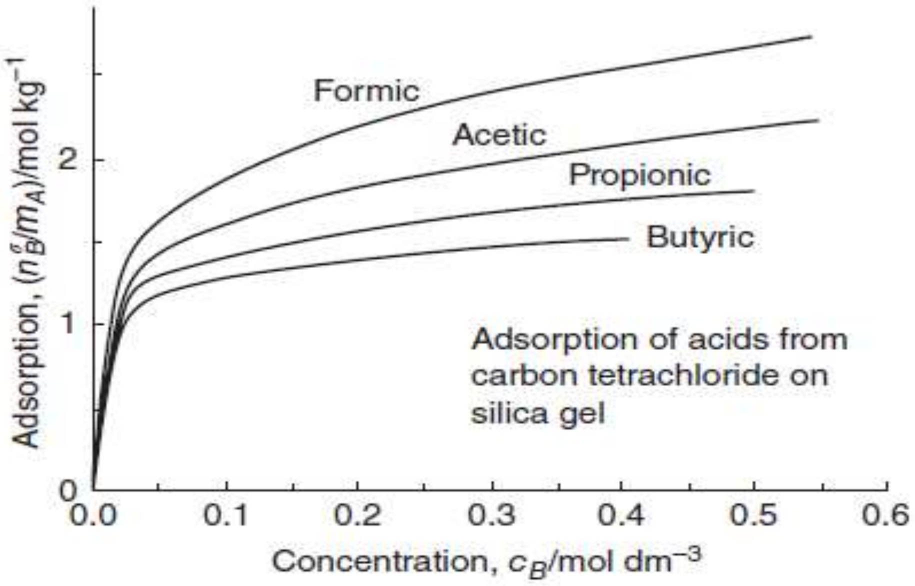
Example: fatty acids – non polar solution

The adsorption sequence is determined by the interaction between the solvent and the alkyl chains.

The longer the chain of acids, the stronger the interaction (i.e. higher affinity) with the non-polar solvent, the more the acid "wants to stay" in the solution and thus the lower the adsorption.



The adsorption of four fatty acids on a polar surface (silica gel) from a non-polar solution (carbon tetrachloride)

Example: Carboxylic acids – aqueous solution

The adsorption of carboxylic acids on a non-polar solid surface (coal) from aqueous solutions increases with increasing chain length.

Thus, the adsorption of valeric acid is much higher than that of butyric acid which in turn is higher than the adsorption of acetic acid.

With increasing chain length, the solubility in water decreases and interaction with the solid surface increases.

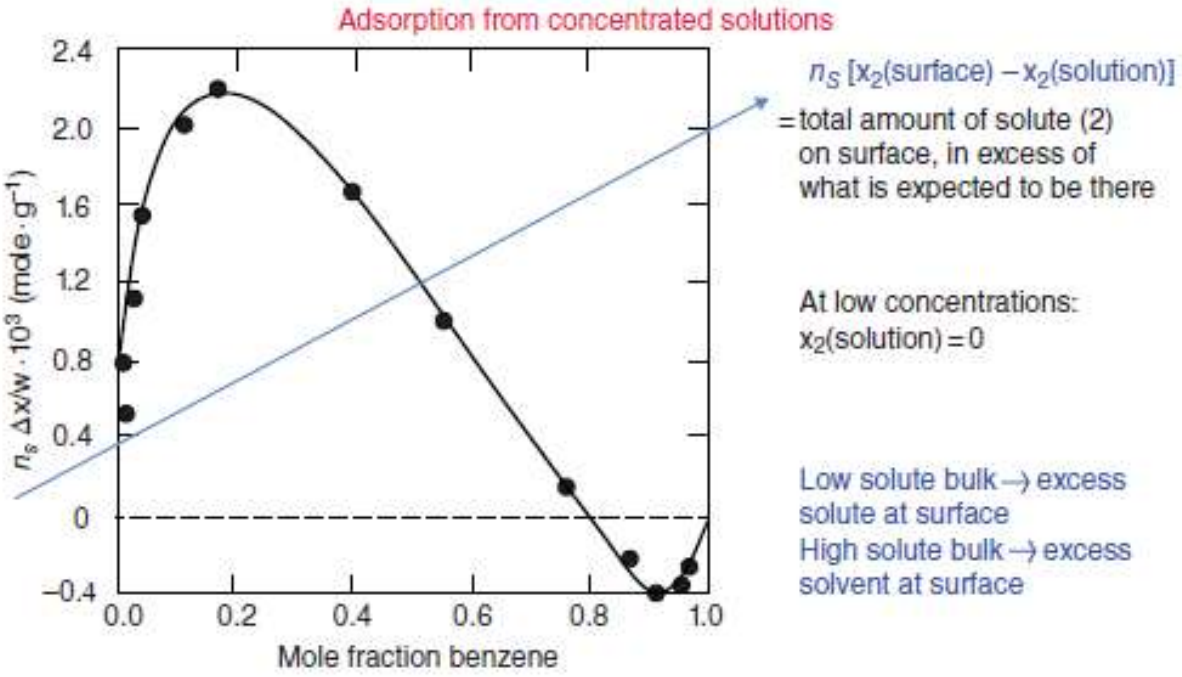
Traube's rule: for each additional methylene group in chain the concentration required to give a certain surface tension is reduced by a factor of 3.

The same rule can be used to predict the effect of chain length on adsorption.

Composite adsorption isotherms

This type of isotherm covers the whole concentration interval, from 100% one component ("solvent") to 100% the other ("solute").

Ordinate: mol adsorbed multiplied by the change in the benzene concentration per g of solid.



$n_S\ [x_2(\text{surface}) - x_2(\text{solution})]$ = total amount of solute (2) on surface, in excess of what is expected to be there

At low concentrations: $x_2(\text{solution}) = 0$

Low solute bulk → excess solute at surface
High solute bulk → excess solvent at surface

In dilute solutions, we have indeed adsorption of benzene, but in concentrated solutions ethanol is adsorbed instead, while benzene is desorbed (negative adsorption). One maximum and one minimum

use

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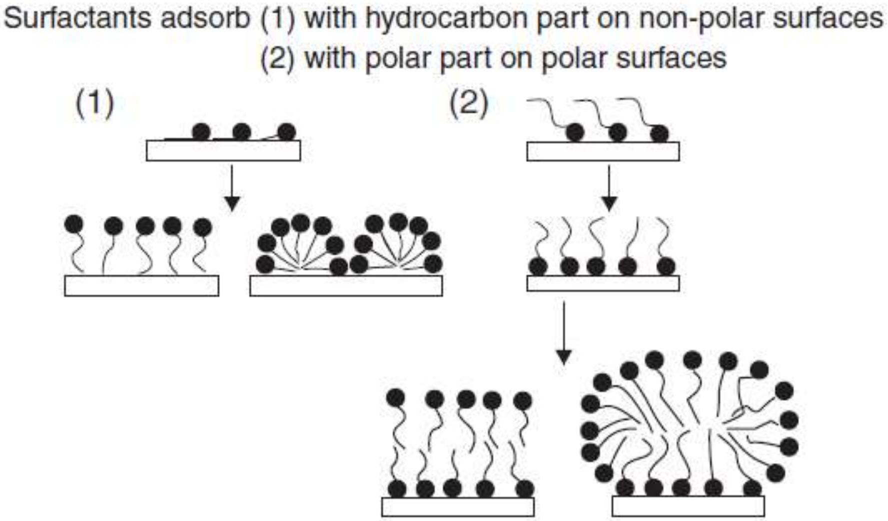
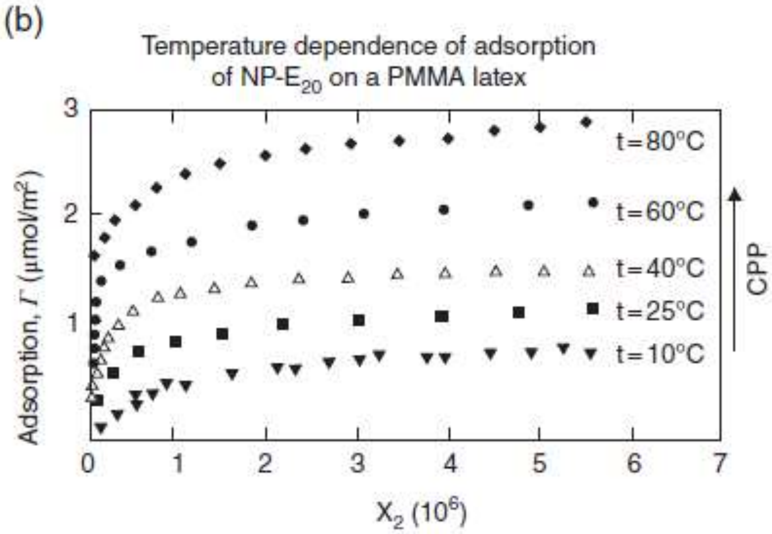
Adsorption of surfactants

The higher the CPP (critical packing parameter) is the higher the adsorption (on hydrophobic surfaces).

All factors that increase CPP (increase of hydrophobic chain or temperature, decrease of hydrophilic length, addition of salt, use of surfactants with two hydrocarbon chains, addition of surfactants with opposite charge, addition of long-chain alcohols or amines, etc.) result in increased adsorption.

Many adsorption isotherms for surfactants, can be well-represented by the Langmuir equation.





Adsorption of polymers

Stability of colloidal dispersion (paints, food, cosmetics, pharmaceuticals, etc.);

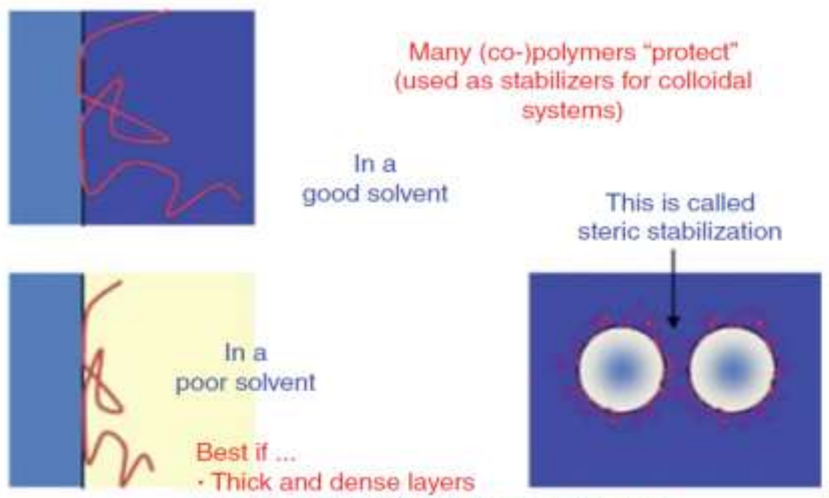
Enhancing instability, e.g. water purification, mineral processing;

Surface modification (hydrophilization), e.g. food processing, bioapplications;

Surface functionalization, e.g. affinity chromatography, bio-tech applications;

Change in properties, e.g. foaming, rheology.

Polymer adsorption and steric stabilization



Many (co-)polymers "protect" (used as stabilizers for colloidal systems)

This is called steric stabilization

Best if ...
- Thick and dense layers
- Good solvents, extended conformations
- Strong adsorption ("firmly anchored") - best from poor solvent
- Complete particle coverage

The adsorption of polymers is very important for understanding and controlling the steric stabilization of colloids

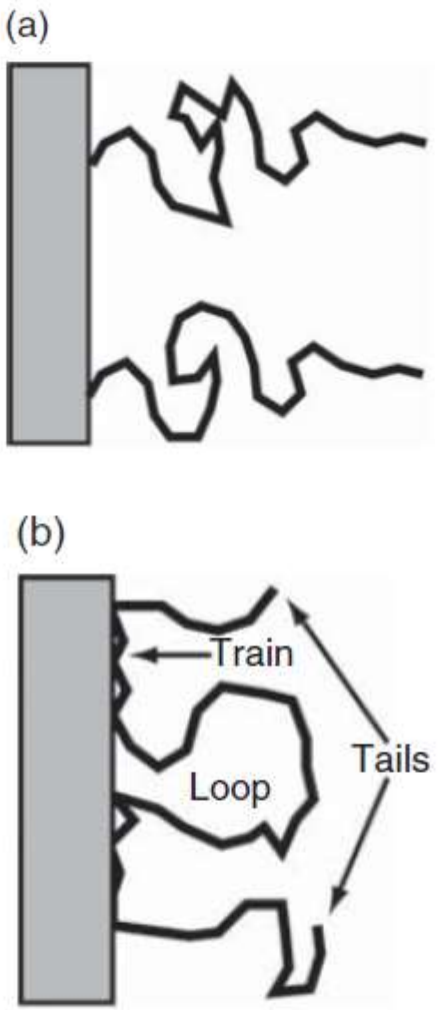
Molecular weight and adsorption. Role of solvent

The adsorption of polymers typically increases with polymer molecular weight and is higher and best (e.g. thicker, denser adsorbed layers) from a solution containing a poor solvent.

The solvent quality influences the adsorption in two ways.

- **The first is by changes in the polymer configuration.**
- **The second way a solvent influences the adsorption**

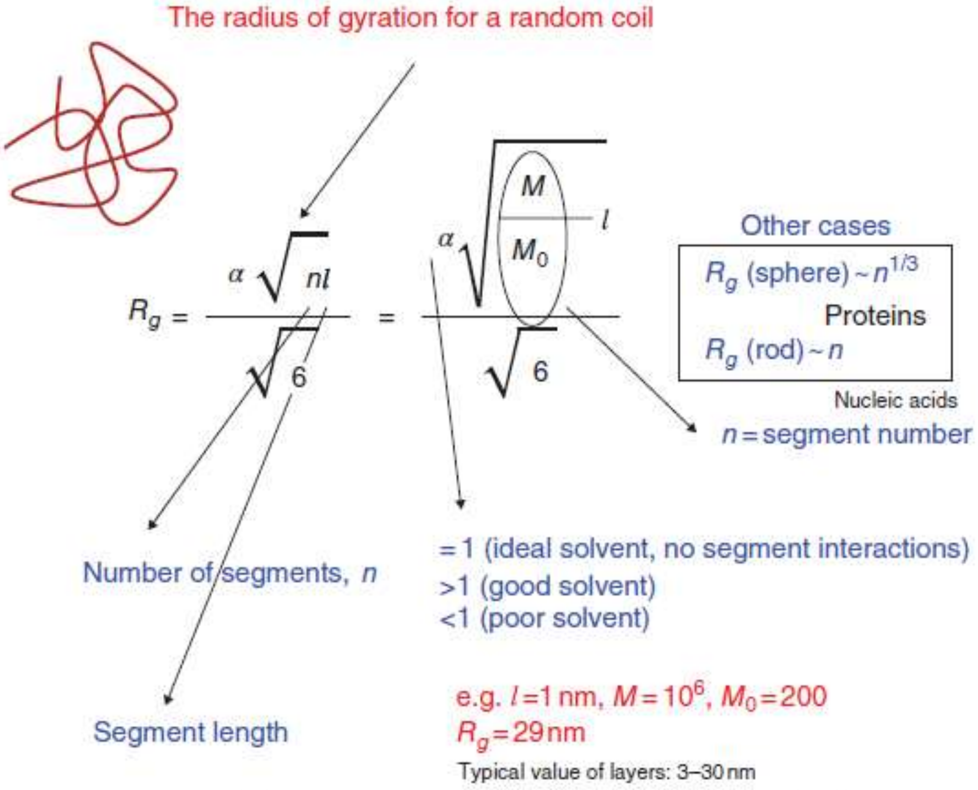
If the polymer is not "happy" in the solution (low stability in solution) it will seek any opportunity to escape the solvent, e.g. by adsorbing on a surface.



Role of the radius of gyration

A measure of the size (extension) of the tails is the so-called radius of gyration, Rg.

This is a very important concept, as two particles repel each other and thus we have steric stabilization only when the distance is about 2Rg (or lower), but the steric force is essentially zero at higher distances.



The radius of gyration for a random coil

$$R_g = \frac{\alpha\sqrt{nl}}{\sqrt{6}} = \frac{\alpha\sqrt{\frac{M}{M_0}\, l}}{\sqrt{6}}$$

Other cases

R_g (sphere) ~ $n^{1/3}$

Proteins

R_g (rod) ~ n

Nucleic acids

n = segment number

Number of segments, n

Segment length

α = 1 (ideal solvent, no segment interactions)

>1 (good solvent)

<1 (poor solvent)

e.g. $l = 1$ nm, $M = 10^6$, $M_0 = 200$

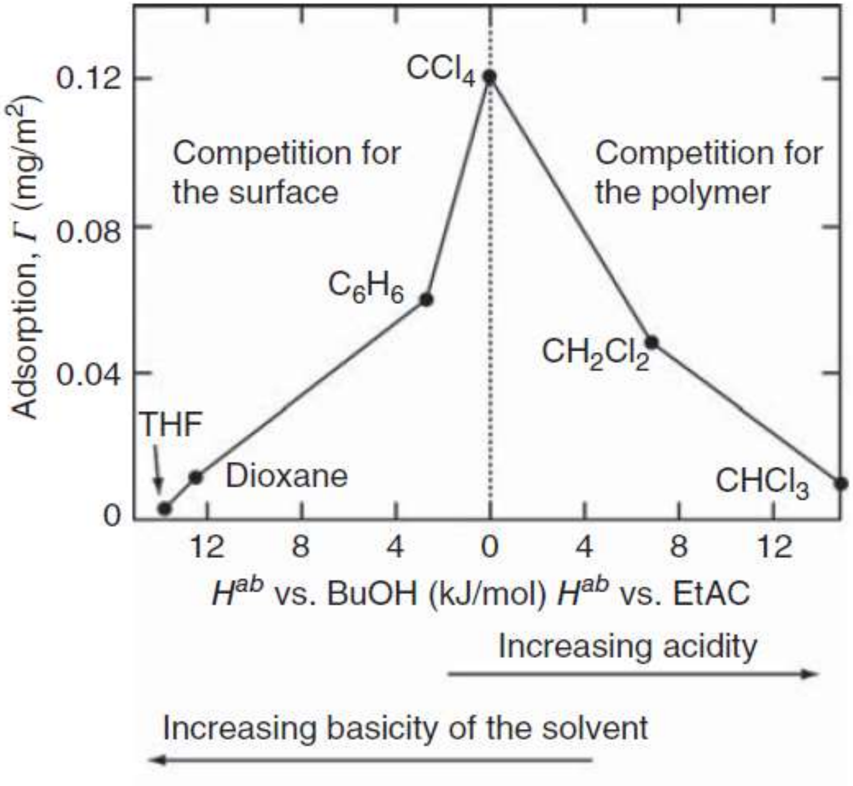
$R_g = 29$ nm

Typical value of layers: 3–30 nm

Lewis acid–Lewis base (LA-LB) concept and polymer adsorption

Very acid solvents compete (with the acidic surface) for the basic polymer and very basic solvents compete (with the basic polymer) for the acidic surface.

It seems that in many cases, solvents of “balanced” acidity/basicity (i.e. not very acid, not very basic, almost neutral) are the best choices for accomplishing maximum adsorption.



The figure illustrates the importance of the Lewis acid–base concept on polymer adsorption onto acidic silica. LB solvents (e.g. benzene, esters, ethers, ketones, etc.) can adsorb on the surface instead of PMMA (poly(methyl methacrylate). In contrast, acid solvents can adsorb on PMMA, prohibiting its adsorption on the surface.

The concept of the Flory–Huggins (FH) - *(X)-parameter*

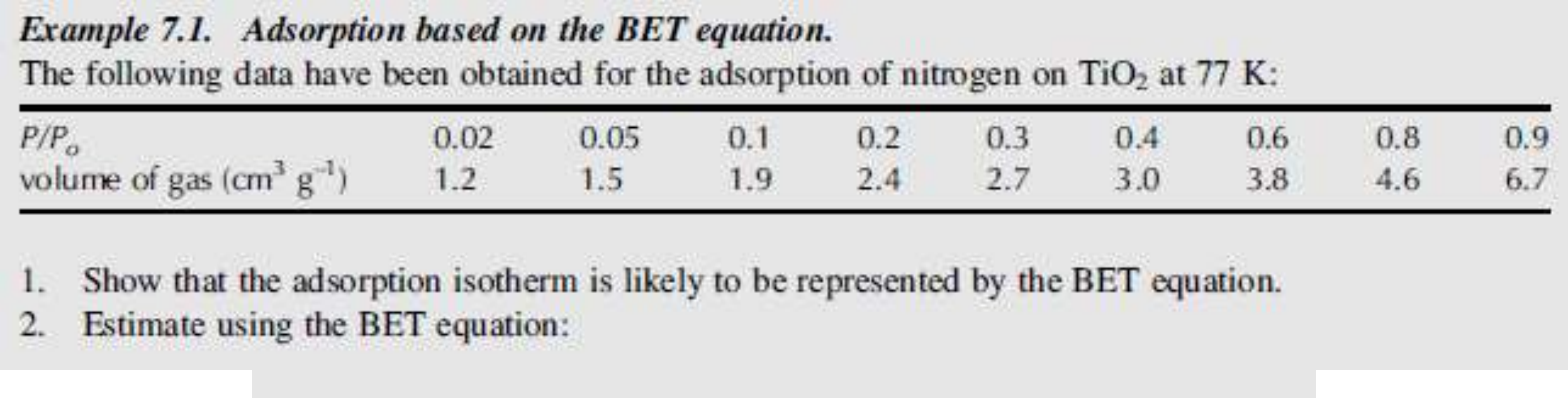
In this way we may assign "χ-values" for the interaction with surface by considering the interaction energies for the polymer–solvent, polymer–surface and solvent–surface.

The polymer will not adsorb if the FH parameter (solvent–polymer) < FH parameter (polymer–surface).

This is because the polymer wants to stay in the solution with a good solvent.

In the opposite case (poor solvent), the polymer will adsorb.

EXAMPLE



Example 7.1. Adsorption based on the BET equation.

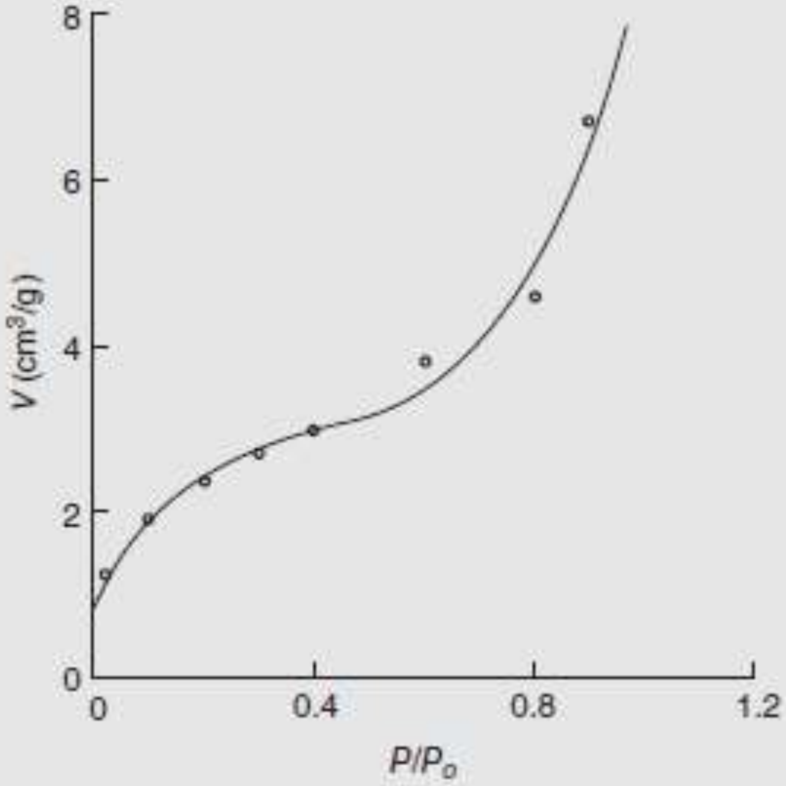
The following data have been obtained for the adsorption of nitrogen on TiO_2 at 77 K:

P/P_o	0.02	0.05	0.1	0.2	0.3	0.4	0.6	0.8	0.9
volume of gas ($cm^3\ g^{-1}$)	1.2	1.5	1.9	2.4	2.7	3.0	3.8	4.6	6.7

1. Show that the adsorption isotherm is likely to be represented by the BET equation.
2. Estimate using the BET equation:

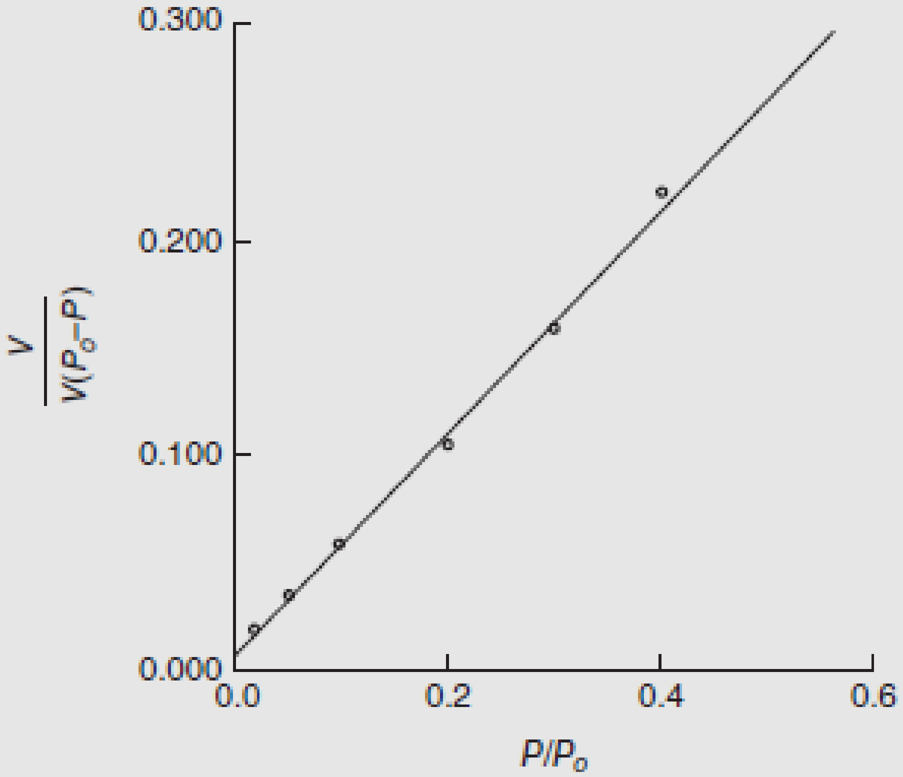
Solution

The *V* versus P/P_o plot clearly shows that the adsorption of nitrogen on titanium oxide has the BET shape.



1. According to the BET theory, the plot of $P/V(P_o - P)$ versus P/P_o should be linear. If we consider all the points provided in the above table, i.e. up to very high pressures, the resulting plot is *not* linear. However, the BET equation should be constructed based only on the points up to reduced pressures of about 0.4, i.e. up to sixth or seventh point. Indeed the plot of $P/V(P_o - P)$ versus P/P_o is linear up to reduced pressure 0.4 (approximately even up to the seventh point of reduced pressure 0.6).

   The straight line is shown in the plot below.



2. The straight line is represented by the equation:

$$P/[V(P_o-P)] = 0.0052999 + 0.526907(P/P_o)$$

(Notice that as only the ratio P/P_o is given, all sides of the fraction $P/[V(P_o-P)]$ should be divided by P_o.)

Then, as known, the volume for monolayer coverage $V_m = 1/(\text{slope} + \text{intercept}) = 1/(0.526907 + 0.0052999) = 1.8789\ \text{cm}^3\ \text{g}^{-1}$.

The specific surface area of solid TiO_2 is then calculated based on this value of V_m as:

$$A_{sp} = \frac{V_m N_A}{V} A_o = \frac{1.8789 \times \left(6.0225 \times 10^{23}\right) \times 16.2.10^{-20}}{22414} = 8.178\text{m}^2\text{g}^{-1}$$

Author, Editor and Referee References

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