

Lecture 4: (Small) Molecular organization: electrokinetics and surfactants

Introduction

In this lecture, we take on the concept of molecular organization focusing on ions and small amphiphilic molecules (charged or not). Larger molecules such as polymers/proteins/DNA will be treated in a different chapter.

The first part of this chapter focuses on ions and on how to couple electric field and moving particles/fluids. This is the so-called field of electrohydrodynamics which includes electrophoresis, electroosmosis and their applications. Thanks to progresses in miniaturization, the production of intense electric fields and effective confinement of molecular assemblies have developed giving rise to many applications such as dielectrophoretic microcytometers, electro-osmotic micropumps, electrophoretic separators,...

Strictly speaking, for electrophoresis to be effective particles/molecules must be charged. In the last part of this chapter we will see that the separation principle can be extended to uncharged species which are transported in self-organized molecular entities made of surfactants and called micelles. The properties of surfactants and their abilities to self-organize are thus briefly presented.

1) Introduction to electrokinetics

1)1) Ionic dissociation and origin of surface charges

Energy of interaction between two elementary charges q_1 and q_2 separated by r :

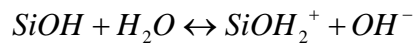
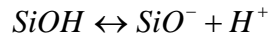
$$U = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r}$$

Charges can therefore dissociate if the thermal energy exceeds electric interaction energy. This happens when charges are separated by a critical length called the Bjerrum length and defined by:

$$r \geq l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r kT}$$

In water (very polar liquid), the Bjerrum length equals 0.7 nm at room temperature.

At the surface of glass, silanol groups (typical distance between 2 groups ~ 0.5 nm) can dissociate giving rise to free mobile ions:

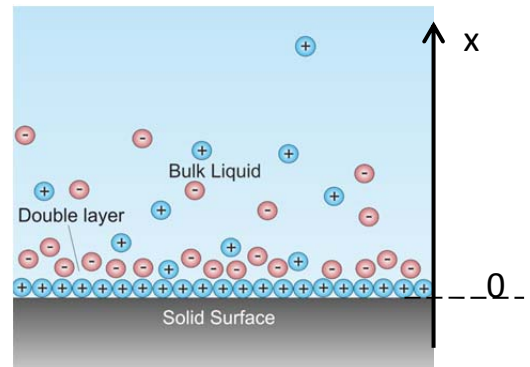


These charges at pH 7 create an electrical potential of the order of -100 mV. Thus it is appropriate to take into account the surface charges for the flow of an electrolyte or a buffer solution in a confined system.

1)2) The electrical double layer or how do these charges spatially distribute?

When an isolated surface carrying an “acquired” charge is immersed in an electrolyte, the mobile charges of the liquid organize themselves and form a double layer near the immersed surface, giving rise to a remarkable structure as illustrated in the figure, right.

Double Layer structure



The first layer is a molecular film of counter ions, which are fixed at the level of the solid/liquid interface under the effect of attractive forces developed by the charged solid surface. This first layer is known as the “Stern layer”. It is bonded to the solid by an electrostatic interaction. The second layer is not bonded to the solid: it is diffuse. The structure of this second layer results from a statistical equilibrium between thermal agitation (which tends to homogenize charge distribution) and electrical forces (which tend to displace charges of opposite signs in opposite directions). The characteristic of this layer can be obtained by using the electrokinetic equations and Poisson’s equation presented in the next section.

It is important to note that solving these equations is self-consistent as the charges create a potential Ψ which influences the distribution of these charges.

We find if ions behave in the potential created by the charged surface as molecules in a perfect gas dilute solutions), that the Debye length defined by $\kappa^{-1} = \frac{\sqrt{\epsilon_0 \epsilon_r kT}}{\sqrt{2c_0 z e}}$ is the typical screening length for electrostatic interactions where c_0 is the ions concentrations far from the solid surface and z the number of elementary charge (e) per ion.

Order of magnitude of the Debye length:

Solution of NaCl @ 10^{-3}M : 10 nm

Solution of NaCl @ 0,1 M (approx. physiological solution :0,15 M): 1 nm

1)3) Some equations: charged particles in an insulating fluid submitted to an electric field

- Coulomb force on an isolated particle of charge q in insulating medium subjected to electric field E :

$$\vec{F}_C = q\vec{E}$$

- Viscous friction on the moving particle of radius R, velocity \vec{V} , surrounding medium viscosity η :

$$\vec{F}_v = -6\pi R\eta\vec{V}$$

→ resulting velocity is $\vec{V} = \mu_e \vec{E}$ with μ_e the electrophoretic mobility defined by $\mu_e = q / 6\pi R\eta$

1)4) Some more equations: Ionic solution in an electric field

Electric current: displacement of charges. These charges can be particles or ions.

We consider three origins of displacement:

(i) Diffusion (see lecture 3, Fick's law) with ρ_e electric charge per unit of volume

$$\vec{J}_D = -D \text{grad} \rho_e$$

(ii) Bulk translation (flow) with \vec{u} the fluid velocity

$$\vec{J}_F = \rho_e \vec{u}$$

(iii) Electric field (\vec{E}) with σ the electrical conductivity

$$\vec{J}_e = \sigma \vec{E}$$

$$\text{Charge conservation} \rightarrow \frac{\partial \rho_e}{\partial t} + \text{div} (\vec{J}_D + \vec{J}_F + \vec{J}_e) = 0 \rightarrow \boxed{\frac{\partial \rho_e}{\partial t} + \vec{u} \cdot \nabla \rho_e = \nabla \cdot (D \nabla \rho_e - \sigma \vec{E})}$$

Additionally, Maxwell's equations (Gauss law) gives an expression for \vec{E} in a media of permittivity ϵ

→ $\text{div} \vec{E} = \frac{\rho_e}{\epsilon}$ and with $\vec{E} = -\nabla \psi$, ψ being the electric potential, it leads to the Poisson's equation:

$$\boxed{\rho_e = -\epsilon \Delta \psi}$$

A fluid with a density of charge ρ_e in the presence of an electric field \vec{E} is subjected to the electrostatic body force density $\vec{f}_{volc} = \rho_e \vec{E}$.

Adding this coulombic force in the classical Navier Stokes, leads to:

$$\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla P + \eta \Delta \vec{u} + \rho_e \vec{E}$$

and for $Re \ll 1$ (micro systems), Stokes equation is replaced by: $\boxed{\nabla P = \eta \Delta \vec{u} + \rho_e \vec{E}}$

2) Applications of electrohydrodynamics

2)1) Electro-osmosis

Definition: the movement of an ionized fluid under the effect of an electric field.

Stokes approximation → $-\nabla P + \eta \Delta \vec{u} + \rho_e \vec{E} = \vec{0}$ with ρ_e determined as in the previous paragraph,

$$\text{leads to: } -\frac{\partial P}{\partial z} + \eta \frac{\partial^2 u}{\partial x^2} - \epsilon E \frac{d^2 \psi}{dx^2} = 0$$

If the pressure gradient is zero: $u(x) = \frac{\epsilon E}{\eta}(\psi - \zeta)$. Away from the double layer, the potential ψ is zero and the velocity of the flow is: $u(x) = \frac{\epsilon \zeta}{\eta} E$. In other words, for distances larger than the Debye length, the flow field induced by an electric potential is a plug flow.

One of the advantages of electro osmosis is the possibility to displace fluids as plug flow preventing Taylor- Aris dispersion which is especially valuable in the field of separation.

2)2) Electrophoresis

Definition: the movement of charged particles by an electric field in a resting fluid (discovered in 1892).

When a charged particle is immersed in an electrolyte, it can no longer be considered to be an isolated charge: in fact, this particle develops a local electric field and reorganizes mobile ions around itself. This behavior establishes a double layer, whose structure is analogous to the one that spontaneously forms near a charged surface. The thickness of this double layer is again the Debye length, typically 10 nm for an immersed particle in an electrolyte.

Two cases can thus be considered (i) the particle size is smaller than the Debye length or (ii) the particle size is greater than the Debye length.

- (i) Ions, small proteins and small strands of DNA $\rightarrow \mu_e = q/6\pi\eta R$ (see section 2.1)
- (ii) Particles are surrounded by the Debye Huckel double layer \rightarrow everything happens in the referential of the particles as in electro-osmosis. The relative velocity with the liquid is $u(x) = \frac{\epsilon \zeta}{\eta} E$ and the mobility of the particles is found to be $\mu_e = \epsilon \zeta / \eta$

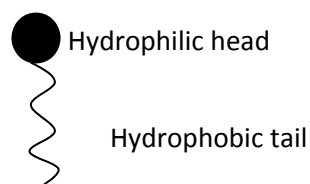
In most of cases, configuration (i) is encountered. One principle use of electrophoresis is to separate ionized molecules which migrate at different velocities within micro canals (capillary electrophoresis) – separation as a function of charge /size ratio.

Remark: electrophoresis can also be used to separate neutral particles \rightarrow micellar capillary electrophoresis. Neutral particles are trapped into micelles form by a ionic surfactant according to their affinity with the hydrophobic tail of the surfactant. Charged micelles are thus separated according to their charge/size ratio allowing separation of different neutral particles.

3) Molecular organization of amphiphilic molecules

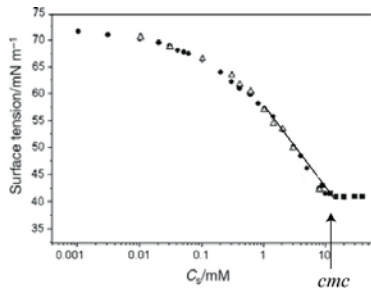
3)1) Structure, CMC and molecular organization

Amphiphilic molecules also called surfactants present the characteristic of having one polarisable/polar/ionic part which is hydrophilic and one hydrophobic part often made of an aliphatic chain.



By placing itself at the interface (between an aqueous solution and air/non polar phase) the amphiphilic character of the molecule is satisfied.

The typical area of a surfactant molecule is in the range of 50 \AA^2 . That means that for 1L of solution exposing an interface of 1 m^2 (huge), the interface is saturated by surfactant molecules for a concentration of approximately 10^{-5} mol/L . Yet, soap solubility is much higher in the range of 1 mol/L , thus the surfactant molecules are not only found at the interface. Indeed above a critical concentration called Critical Micellar Concentration (CMC), surfactant molecules form aggregates or micelles.



In other words, surface tension decreases as surfactant concentration increases till the critical micellar concentration (cmc) has been reached. The cmc is the concentration for which all added molecules condensate as aggregates – no more free surface is available at the interface to place additional polar heads.

Ritacco et al (2000)

3)2) Molecular organization: assemblies geometry

The shape and size of the "aggregate" depends on the details of the molecule.

In practice, it is found that spherical micelles are reasonably monodisperse. Random collection of spherical micelles of all sizes is never observed in practice. The micelles size is determined by the competition between:

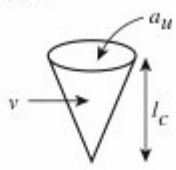


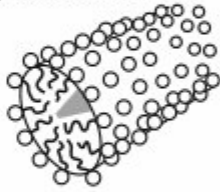



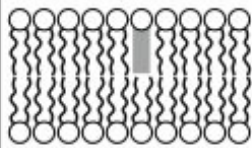

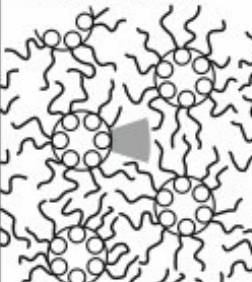
- (i) polar repulsions between polar heads and,
- (ii) steric repulsion of apolar chains

The balance between these two competing contributions fixes the optimal size of spherical micelles



Source: <http://biologicalphysics.iop.org>

These molecular assemblies are not only spherical (micelles) but can take various forms depending on the relative importance of the size of the polar head a , the length of the apolar tail l and v the volume such a tail occupies.

Lipid	Critical packing parameter $v/a_u l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: <i>SDS in low salt</i>	$<1/3$	Cone 	spherical micelles 
Single-chained lipids with small head-group areas: <i>SDS and CTAB in high salt, non-ionic lipids</i>	$1/3-1/2$	Truncated cone 	cylindrical micelles 
Double-chained lipids with large head-group areas, fluid chains: <i>phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG^a, dihexadecyl phosphate, diakyl dimethyl ammonium salts</i>	$1/2-1$	truncated cone 	flexible bilayers, vesicles 
Double-chained lipids with small head-groups areas, anionic lipids in high salt, saturated frozen chains: <i>phosphatidyl ethanolamine, phosphatidyl serine + Ca²⁺</i>	~ 1	cylinder 	planar bilayers 
Double-chained lipids with small head-group areas, nonionic lipids, poly (<i>cis</i>) unsaturated chains, high <i>T</i> : <i>Unsaturated phosphatidyl ethanolamine, cardiolipin + Ca²⁺, phosphatidic acid + Ca²⁺, cholesterol, MGDG^b</i>	>1	inverted truncated cone or wedge 	inverted micelles 

^aDGDG, digalactosyl diglyceride, diglucosyl diglyceride
^bMGDG, monogalactosyl diglyceride, monoglucosyl diglyceride

Source: <http://biologicalphysics.iop.org>

Remark: Aggregation involves a decrease in entropy of surfactant molecules, so can occur only if there is a significant overall decrease in free energy. The enthalpic terms are not sufficient to compensate this loss; the gain of solvent entropy (around polar heads) is the driving force of molecular assemblies of surfactants and is also referred to as hydrophobic interactions.

3)3) Characteristic numbers

Molecular weight:

Typically between 200g/mol and 1000 g/mol

For smaller molecules, the electrostatic interactions at the polar head are much stronger than hydrophobic forces → they dissolve in water

For larger molecules, the hydrophobic interactions of the apolar tails are much stronger than the interactions of polar heads → phase separation occurs

Remark: larger amphiphilic molecules exist but they have then a different structure (no polar head): copolymer having a hydrophilic block and a hydrophobic one. Various microphases are observed depending on the details of the macromolecules.

Partition coefficient:

Used to describe the relative affinity for both media; P is the partition coefficient between octanol and water; log P is often used by biologists and pharmacists.

Small log P → hydrophilic

Large log P → hydrophobic

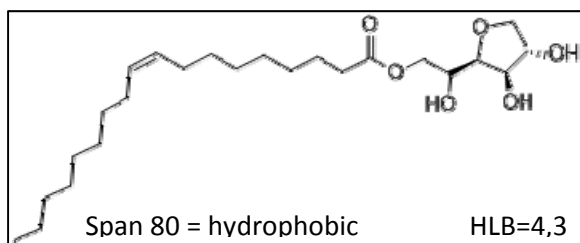
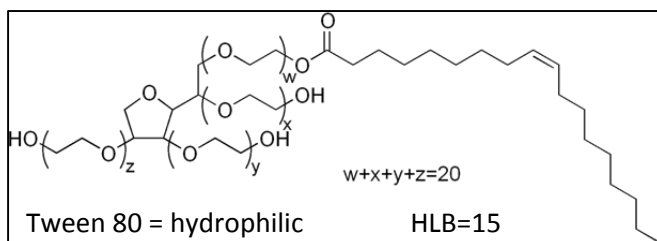
Hydrophilic Lipophilic Balance (HLB):

Used to describe the relative affinity for both media; it is an arbitrary scale varying between 0 (hydrophilic) and 20 (hydrophobic)

Large HLB → hydrophilic

Small HLB → hydrophobic

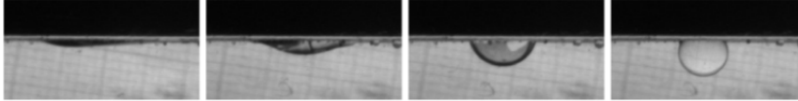
Examples



3)4) Applications

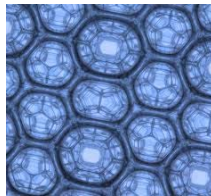
In practice, surfactants are used to lower surface tension from typically 60mN/m down to 30mN/m. They can be used:

- for detergency, see picture below:



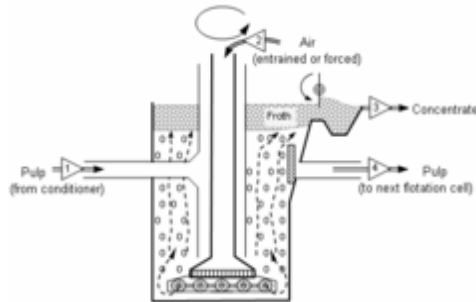
Agut&Damiens (2008)

- to stabilize dispersion (emulsion, foam, suspension)



Gabrielli & Brakke (2012)

- for flotation (froth flotation, waste water treatment)



Source

Wikipedia

- for micellar capillary electrophoresis

Lipids are also used to create vesicles, liposomes to carry drugs or contrast agent, to increase bio availability of drugs via for example micro-emulsion, reversible emulsions, self emulsifying systems,...