Surface and Colloid Chemistry

คม 363 เคมีเชิงฟิสิกส์ 3

สาขาวิชาเคมี

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CH 363 Physical Chemistry 3

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What is Surface Chemistry?

Molecules at interfaces behave differently than bulk.

Liquid surfaces

Surfaces of oceans, lakes, and rivers

Lung surface, biological cells surfaces

Solid surfaces

Road surfaces (car tire)

Adhesion, glues, tapes

Liquid-solid interfaces

Washing and cleaning (dry cleaning)

Wastewater treatment

Air pollution

Power plants

Liquid–liquid interfaces (oil–water systems)

Emulsions (cosmetics, pharmaceutical products)

Diverse industries

Oil and gas, and shale oil recovery (fracking technology), paper and printing, milk products

What are colloids?

Colloids (the Greek word for "glue-like") are a wide variety of systems consisting of finely divided particles or macromolecules (such as, glue, gelatin, proteins) which are found in everyday life.

- 1. Simple colloids, clear distinction can be made between the disperse phase and the disperse medium, for example, simple emulsions of oil-in-water(O/W) or water-in-oil (W/O).
- 2. Multiple colloids involve the coexistence of three phases of which two are finely divided, for example, multiple emulsions (mayonnaise, milk) of water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O).
- 3. Network colloids have two phases forming an interpenetrating network, for example, polymer matrix.

Colloids are homogeneous mixtures.

Suspensions are heterogeneous mixtures.

TABLE 12.10 Comparison of Solutions, Colloids, and Suspensions						
Type of Mixture	Type of Particle	Settling	Separation			
Solution	Small particles such as atoms, ions, or small molecules	Particles do not settle	Particles cannot be separated by filters or semipermeable membranes			
Colloid	Larger molecules or groups of molecules or ions	Particles do not settle	Particles can be separated by semipermeable membranes but not by filters			
Suspension	Very large particles that may be visible	Particles settle rapidly	Particles can be separated by filters			

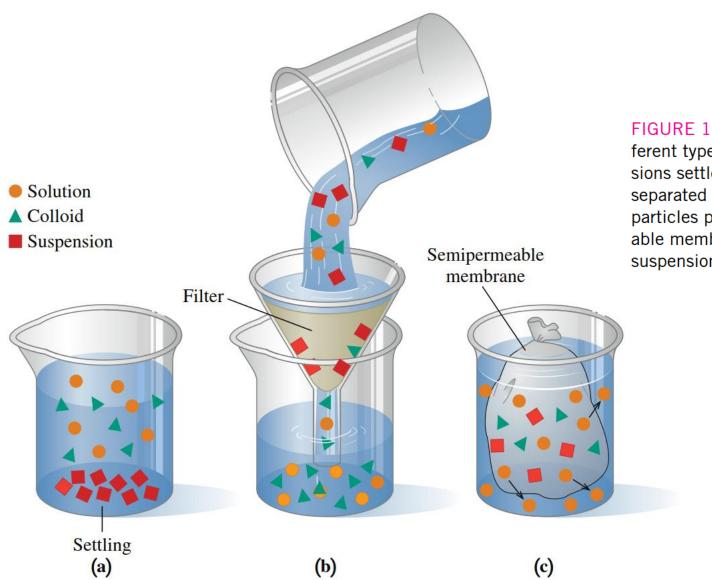


FIGURE 12.10 Properties of different types of mixtures: (a) suspensions settle out; (b) suspensions are separated by a filter; (c) solution particles pass through a semipermeable membrane, but colloids and suspensions do not.

Colloids or Colloidal dispersions

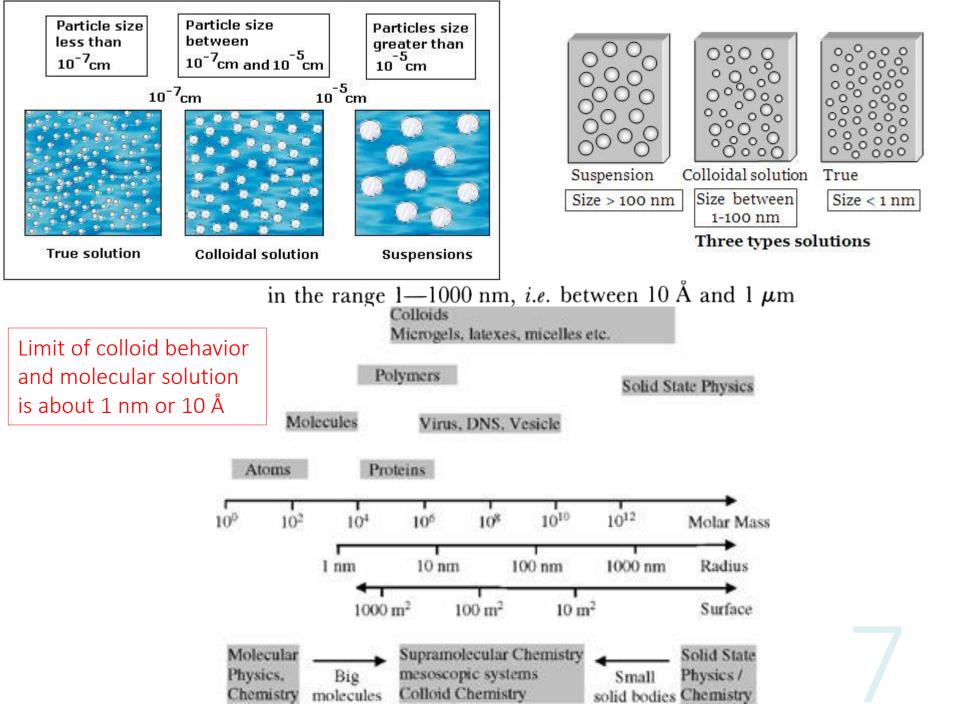
Large molecules, proteins, group of molecules, or ions.

Colloids are <u>homogeneous</u> mixtures.

TABLE 12.9 Examples of Colloids

	Substance Dispersed	Dispersing Medium	
Fog, clouds, sprays	Liquid	Gas	Aerosols
Dust, smoke	Solid	Gas	Smog
Shaving cream, whipped cream, soapsuds	Gas	Liquid	Foam
Styrofoam, marshmallows	Gas	Solid	TOalli
Mayonnaise, homogenized milk, hand lotions	Liquid	Liquid	Emulsions
Cheese, butter	Liquid	Solid	
Blood plasma, paints (latex), gelatin	Solid	Liquid	Biocolloid

Simple colloids (2 phases), Multiple colloids (≥3 phases), Network colloids (gels, porous solids)



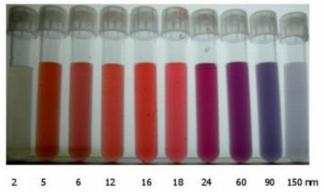
Colloid science is interdisciplinary

Knowledge of different areas of science including physical chemistry, physics, mathematics, and also

structural biology.

Liposome

Different sizes of colloidal gold particles



Micelle

Bilayer sheet

Colloids, Micelles, Biological Membranes

Colloids

Suspension → Colloid → Solution

Micelles

Critical Micelle Concentration (CMC)

Biological membranes

Lipid bi-layers

Colloid nomenclature/ classification

Name depends on the phases involved.

Sol = dispersion of solid in liquid (Au cluster in H_2 0) or solid in solid (Au in glass, ruby glass)

Aerosol = dispersion of solid/liquid in gas

Emulsion = dispersion of liquid in liquid (e.g. milk)

Foam = dispersion of gas in liquid/solid

Gel = semirigid mass of lyophilic sol

Colloid nomenclature/ classification

Colloids can also be grouped according to their interaction with solvent it is dispersed in.

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Lyophilic = solvent attracting (-philic, like) colloid usually similar to solvent e.g. –OH group, H-bonding
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Lyophobic = solvent repelling (-phobic, hate) e.g. metal sols
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If the solvent is water, Hydrophilic and Hydrophobic terms are used instead.

How do we create colloids

Aerosol – Sneezing!

Tear away spray of liquid with jet of gas. If the liquid is charged, dispersion is aided by electrostatic repulsion.

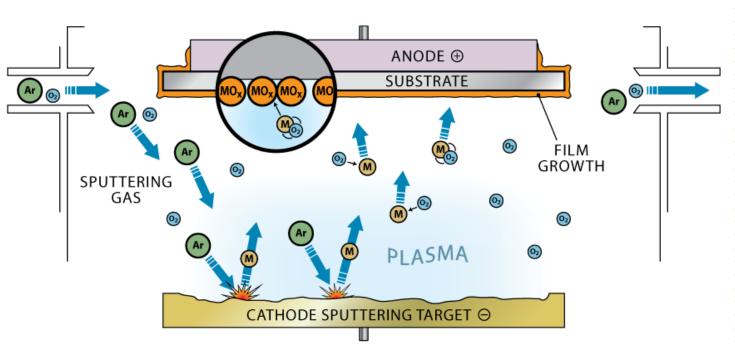




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How do we create colloids

Electric current – sputtering of electrode into particles Chemical peptizing agent – Agl dispersed by adding KI



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How do we create colloids

Shaking vigorously can create emulsions, but we need emulsifying agent or emulsifier to stabilize product. This can be soap or other surfactants or a lyophilic sol that forms a protective film around dispersed phase.

Milk – emulsion of fats in water with casein as the emulsifier. Cream floating on top of milk means that casein is not always completely successful

Colloid particle size

The particle size distribution (PSD) directly affects the bioavailability of active pharmaceutical ingredients.

As with suspensions, colloidal dispersions also contain a range of sizes and, hence PSD.

Colloidal Dispersions	Size Range (nm–10 μ)	
Mist/fog	$0.1~\mu{-}10~\mu$	
Pollen/bacteria	$0.1~\mu{-}10~\mu$	
Oil in smoke/exhaust	$1~\mu$ – $100~\mu$	
Virus	1 nm–10 μ	
Polymers/macromolecules	0.1 nm-100 nm	
Micelles	0.1 nm-10 nm	
Vesicles	$1~\mu{-}1000~\mu$	

Structure and stability

Colloids usually thermodynamically unstable, but kinetically nonlabile (stable).

Unstable – separation of particles in short time

Stable – last for a very long time, e.g. > 1 year

Metastable – in between the two states

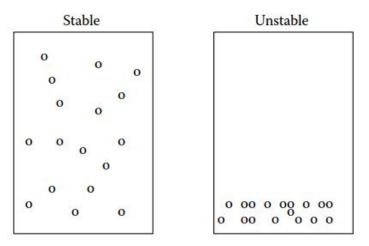


FIGURE 7.2 Stable wastewater suspension of particles and unstable suspension after suitable pH adjustment and other additives. (See text for details.)

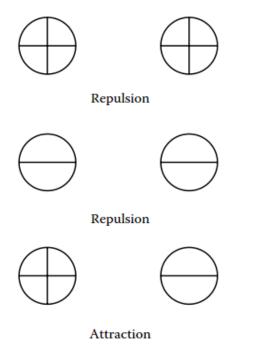
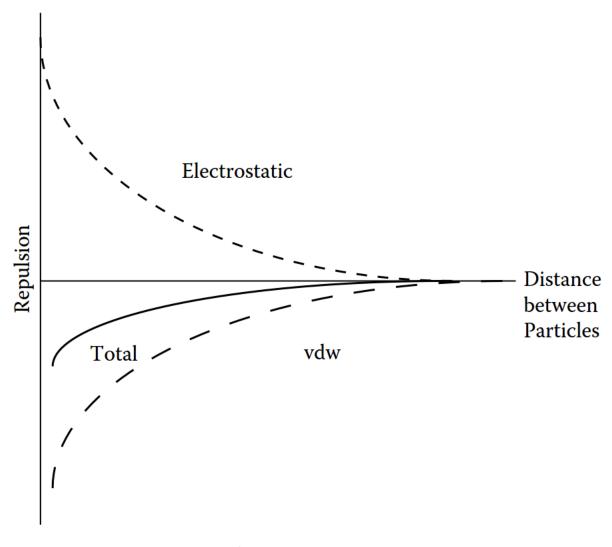


FIGURE 7.3 Solid particles with charges: positive–positive (repulsion), negative–negative (repulsion), and positive–negative (attraction).

Colloid particles attract and repel each other

Various forces involved depending on distance between colloid particles

- Van der Waals
- Electrostatic
- Steric
- Hydration
- Polymer–polymer interactions



Attraction

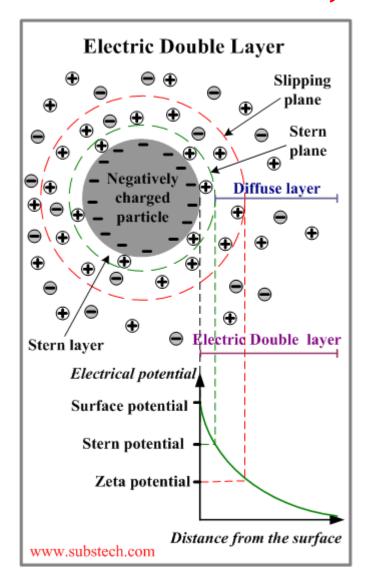
Variation of repulsion and attraction forces versus distance

Electric Double Layer (EDL)

Electric Double Layer is the layer surrounding a particle of the dispersed phase and including the ions adsorbed on the particle surface and a film of the countercharged dispersion medium.

The Electric Double Layer is electrically neutral and can be divided into three parts.

Electric double layer (schematic)



- Surface charge charged ions (commonly negative) adsorbed on the particle surface.
- Stern layer counterions (charged opposite to the surface charge) attracted to the particle surface and closely attached to it by the electrostatic force.
- Diffuse layer a film of the dispersion medium (solvent) adjacent to the particle. Diffuse layer contains free ions with a higher concentration of the counterions. The ions of the diffuse layer are affected by the electrostatic force of the charged particle.

Electric Double Layer- zeta potential

When a colloidal particle moves in the dispersion medium, a layer of the surrounding liquid remains attached to the particle. The boundary of this layer is called slipping plane (shear plane).

The value of the electric potential at the slipping plane is called **Zeta potential**, which is very important parameter in the theory of interaction of colloidal particles.

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Why is the electric double layer important?

The primary role of the electric double layer is to confer kinetic non-lability (ความสถียร). Colliding colloidal particles break through the double layer and coalesce only if the collision is sufficiently energetic to disrupt the layers of ions and solvating molecules

...or if thermal motion has stirred away the surface accumulation of charge. This disruption may occur at high temperatures, which is one reason why sols precipitate when they are heated.

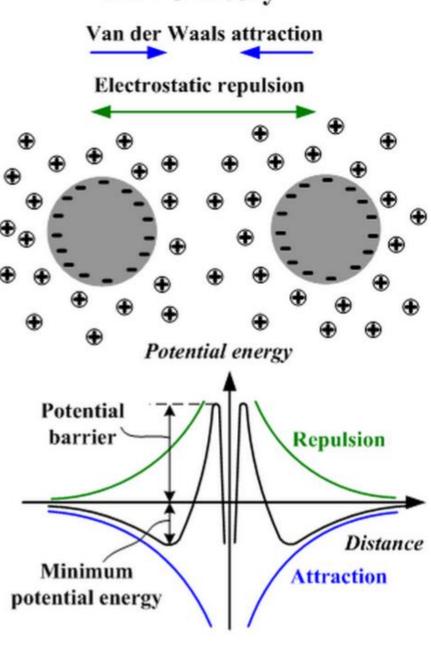
DLVO theory – stability of colloids

In 1940s Deryagin, Landau, Vewey and Overbeek developed a theory of the stability of colloidal systems (DLVO theory).

There is a balance between

- repulsive interaction between the charge of the EDL on the neighbouring particles and
- + attractive interactions from van del Waals forces between the molecules of the particles

DLVO theory



$$V_{\text{repulsion}} = +\frac{Aa^2\zeta^2}{R}e^{-s/r_D}$$

A is a constant ζ = the zeta potential R = the separation of centres s = the separation of the surfaces of the two particles (s = R - 2a for spherical particles of radius a) r_D = the thickness of the double layer. This expression is valid for small particles with a thick double layer (a << rD).

Flocculation (การสมานตะกอน) vs Coagulation (การรวมตะกอน)

<u>Flocculation</u> is the aggregation of the particles. Flocculated material can often be redispersed by agitation because the well is so shallow.

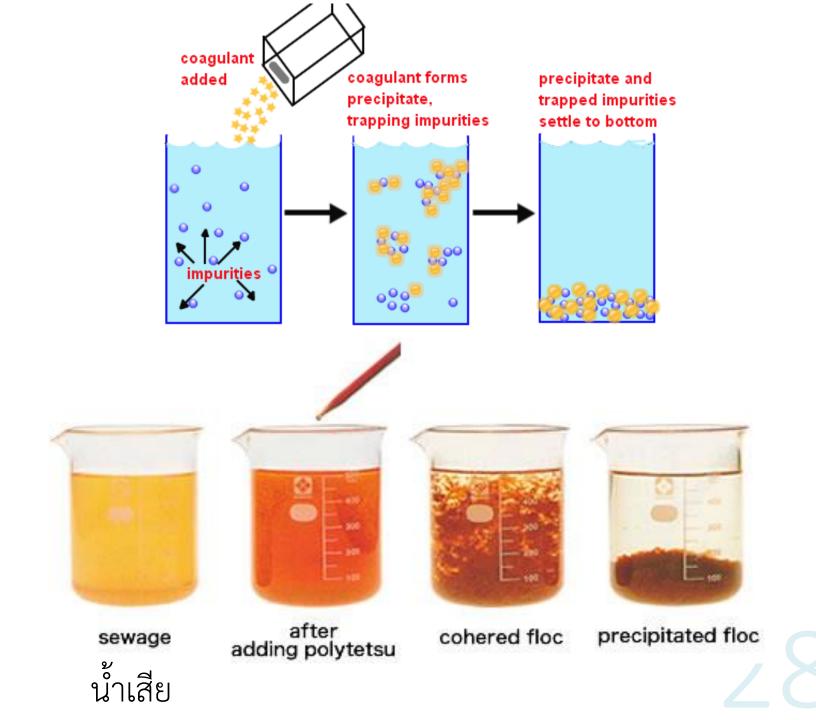
<u>Coagulation</u> is the irreversible aggregation of distinct particles into large particles, occurs when the separation of the particles is so small that they enter the primary minimum of the potential energy curve and van der Waals forces are dominant.

Flocculating agents

The ionic strength of a solution is increased by the addition of ions, particularly those of high charge type, so such ions act as flocculating agents.

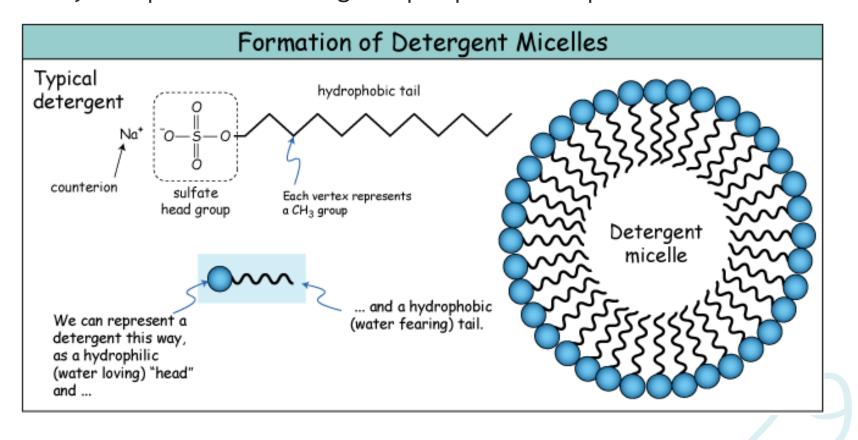
Hydrophobic colloids are flocculated most efficiently by ions of opposite charge type and high charge number. The Al^{3+} ions in alum (สารส้ม) $KAl(SO_4)_2 \cdot 12H_2O$ are very effective, and are used to induce the congealing (การจับตัวกัน) of blood.

An Alum Block sold as an <u>astringent</u> in pharmacies in India



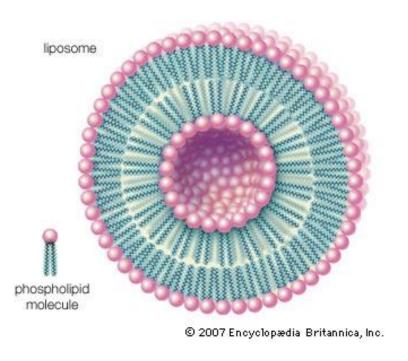
Micelles – colloid sized cluster of molecules

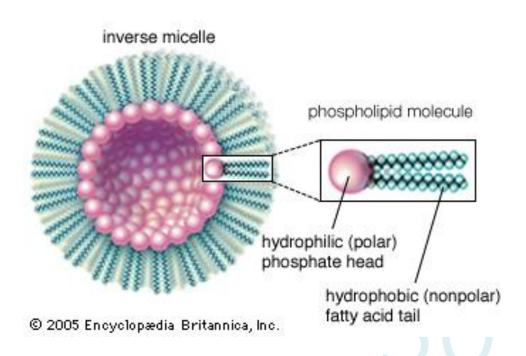
In aqueous solutions surfactant molecules or ions can cluster together as micelles. Hydrophobic tails join and their hydrophilic head groups provide protection.



Liposomes and Inverse Micelles

Phospholipids can be used to form artificial structures called liposomes, which are double-walled, hollow spheres useful for encapsulating other molecules such as pharmaceutical drugs.



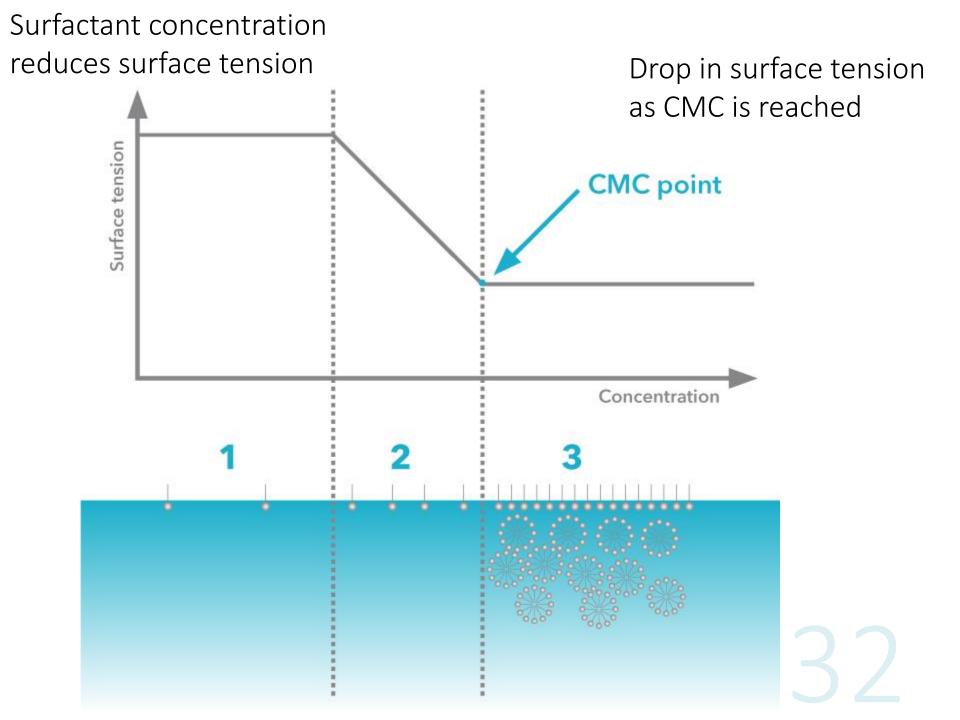


Micelle formation

Micelles form only above the critical micelle concentration (CMC) and above the Kraft temperature.

The CMC is detected by noting a pronounced change in physical properties of the solution, particularly the molar conductivity.

Kraft temperature is the minimum temperature at which surfactants form micelles, below this and no micelles form.



Actual CMC properties

There is no abrupt (sudden) change in properties at the CMC; rather, there is a transition region corresponding to a range of concentrations around the CMC where physical properties vary smoothly but nonlinearly with the concentration.

The hydrocarbon interior of a micelle is like a droplet of oil and NMR studies show that the hydrocarbon tails are mobile, but more restrictive than in bulk.

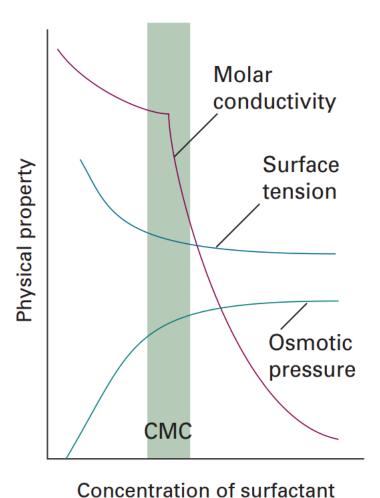


Fig. 18.24 The typical variation of some physical properties of an aqueous solution

of sodium dodecylsulfate close to the critical micelle concentration (CMC).

Why are Micelles important?

Micelles are important in industry and biology on account of their solubilizing function: matter can be transported by water after it has been dissolved in their hydrocarbon interiors.

For this reason, micellar systems can be used in various fields such as:

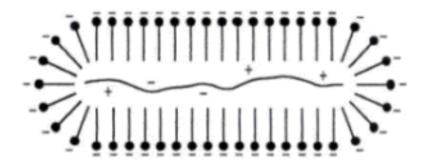
- detergents
- organic synthesis
- > froth (ฟองโฟม) flotation
- > petroleum recovery

Different types of micelles

Non-ionic surfactant molecules may cluster together in clumps of 1000 or more,

but ionic species tend to be disrupted (destroyed) by the electrostatic repulsions between head groups and are normally limited to groups of less than about 100.

However, the disruptive effect depends more on the effective size of the head group than the charge.



Surfactant parameter

The micelle population is often polydisperse, and the shapes of the individual micelles vary with shape of the constituent surfactant molecules, surfactant concentration, and temperature.

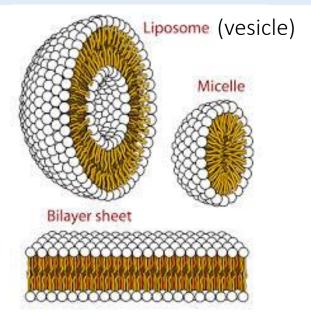
A useful predictor of the shape of the micelle is the surfactant parameter,

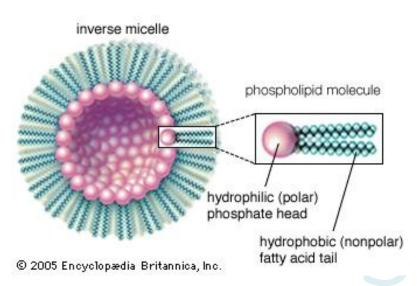
$$N_{\rm s} = \frac{V}{Al}$$

where V is the volume of the hydrophobic surfactant tail, A is the area of the hydrophilic surfactant head group, and I the maximum length of the surfactant tail.

Table 18.1 Variation of micelle shape with the surfactant parameter

Value or range of the surfactant parameter, N_s	Micelle shape
< 0.33	Spherical
0.33 to 0.50	Cylindrical rods
0.50 to 1.00	Vesicles
1.00	Planar bilayers
> 1.00	Reverse micelles and other shapes





What is surface chemistry?

Molecules at or near the <u>surface</u> will interact differently from those in the <u>bulk</u>.

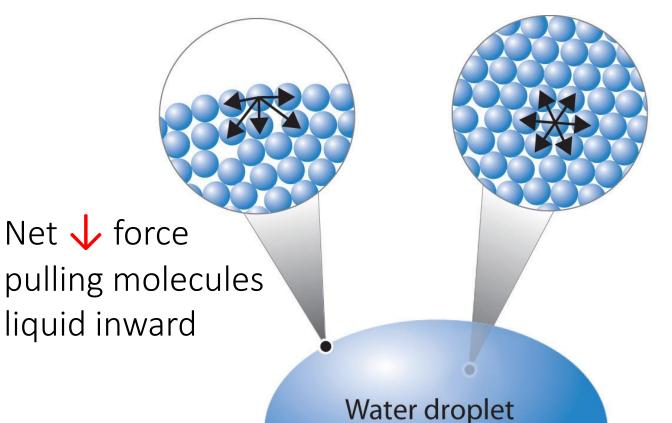
Adhesion (different molecules) and

Cohesion (same molecules) forces.

The interfacial region is found to be of molecular dimension. Some experiments show it to be of one or few molecules thick.

What is surface chemistry?

A molecule of a liquid attracts the molecules that surround it and in turn it is attracted by them.



No net force.

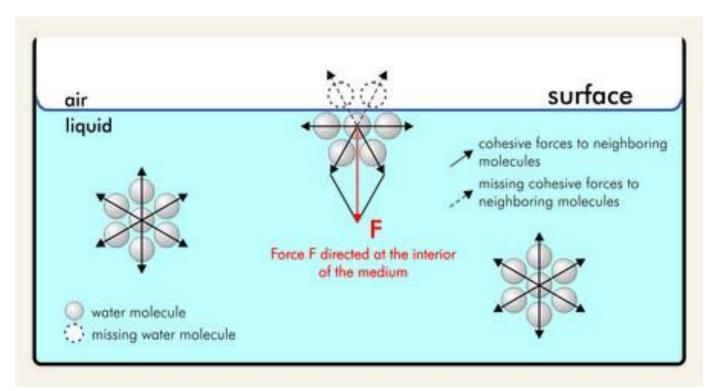
Molecule moves

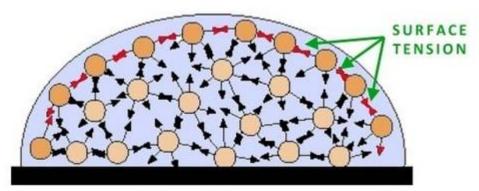
more freely

 $H_2O - H_2O$ (cohesion)

H₂O – surface (adhesion)

Surface tension: Why does it occur?





A fluid surface behaves like an elastic membrane









Surface tension determines shape of droplet





Surface tension (definition)

The energy required to increase the surface area of a liquid by a specific amount;

Joules per square meter (J/m²) or dyne per centimeter (dyn/cm)

$$\gamma = 1 \frac{\text{dyn}}{\text{cm}} = 1 \frac{\text{erg}}{\text{cm}^2} = 1 \frac{\text{mN}}{\text{m}} = 0.001 \frac{\text{N}}{\text{m}} = 0.001 \frac{\text{J}}{\text{m}^2}$$

Surface tension depends on intermolecular forces

The stronger the intermolecular forces, the higher the surface tension. For example,

Water has strong intermolecular hydrogen bonding, and one of the highest surface tension values of any liquid.

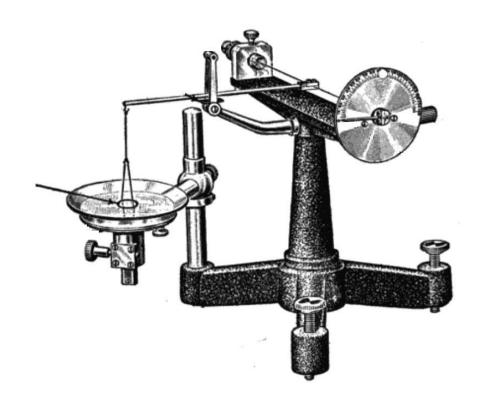
Low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions.

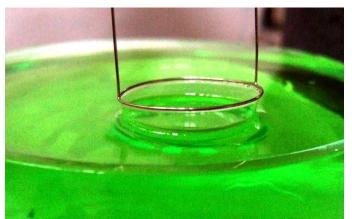
Surface tension of selected liquids

			<u> </u>	
Substance	Surface Tension (× 10 ⁻³ J/m ²)	Viscosity (mPa·s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organics				
diethyl ether	17	0.22	531	34.6
<i>n</i> -hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	_
20°C	72.8	1.00	17.5	_
60°C	66.2	0.47	149	-1
100°C	58.9	0.28	760	-41

Tensiometer – surface tension measurement

Various machines can be used Du Noüy-Padday Rod Pull

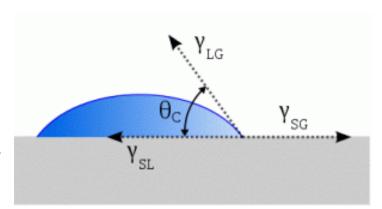




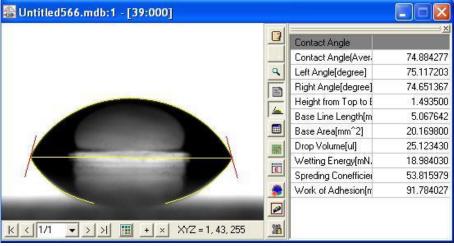


Goniometer/Tensiometer

Measures contact angle (θ) and Surface tension in same machine.



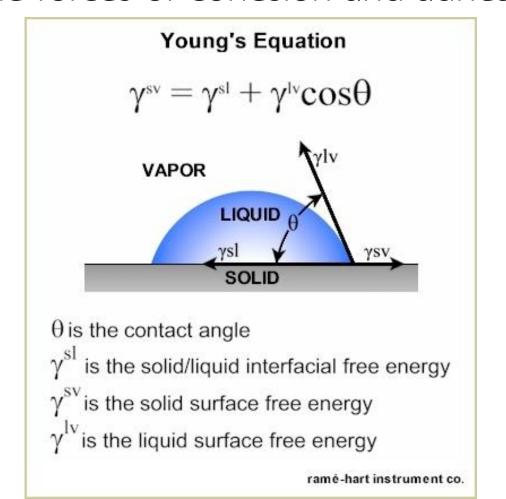




CCD camera takes digital images

Surface energy measurements

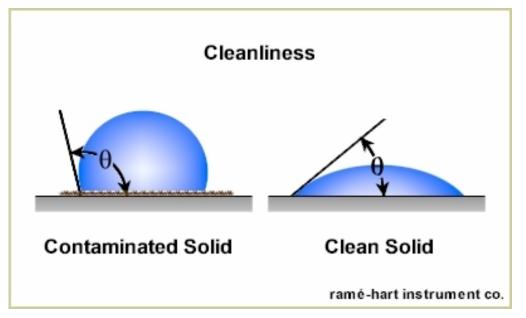
Young's equation is used to describe the interactions between the forces of cohesion and adhesion



Contact angles \rightarrow information about surfaces

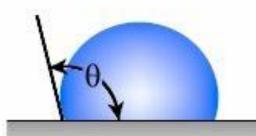
Organic contaminants will prevent wetting and result in higher contact angles on hydrophilic surfaces.

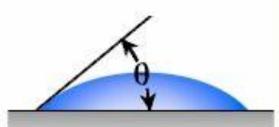
As a surface is cleaned and treated to remove contaminants the contact angle typically will decrease as wetting improves and surface energy increases.



Hydrophobic Surface

Hydrophilic Surface

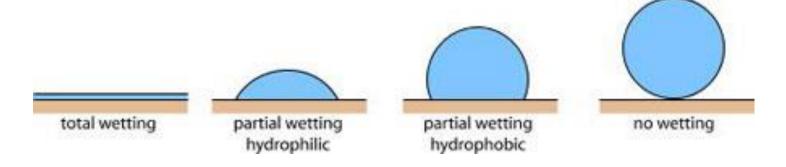


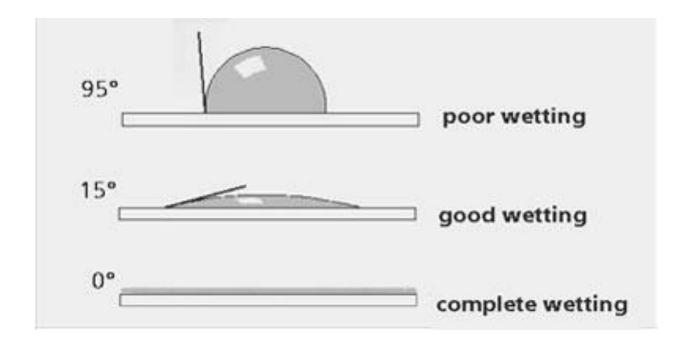


high poor poor low contact angle adhesiveness wettability solid surface free energy low good good high

ramé-hart instrument co.

Wetting of surfaces





What are surfactants? สารลดแรงตึงผิว

Surfactants or surface active agents affect the properties of a surface and promote dispersion of various phases, e.g.

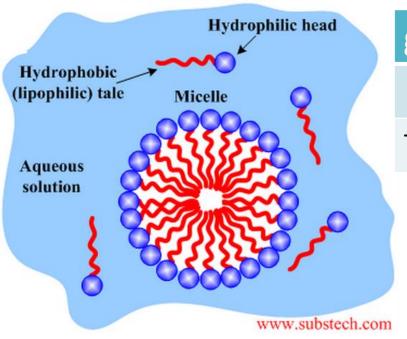
- emulsification of oils (liquid phase)
- suspension of solid residues (solid phase)
- foaming (gaseous phase)

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water.

Surfactants are amphiphilic molecules

Due to their amphiphilic (double-love) nature surfactant molecules are repealed to the interface in any solvent (either polar or non-polar)

Amphiphilic surfactant molecular structure



group	Water	Fat/oil
Head	Hydrophilic	Lipophobic
Tail	Hydrophobic	Lipophilic

Philic – like

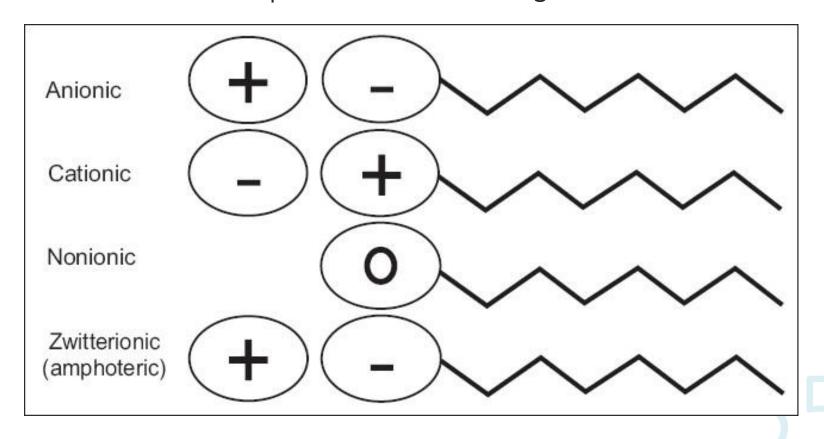
Phobic – hate

Hydro – water

Lipo – fat

Surfactant classification (+, -, neutral)

Surfactants function by breaking down the interface between water and oils and/or dirt and hold these oils and dirt in suspension, allowing their removal.

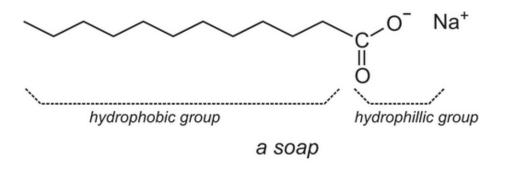


Anionic surfactants: Definition

Dissociate in aqueous solutions into:

- > amphiphilic organic anion (negatively charged ion)
- small inorganic cation (positively charged ion: Na⁺, K⁺)

Anionic surfacants are generally non-toxic and are the most widely used type of surfactant.



Anionic surfactants: Exmaples

Based on the straight chain alkylbenzene sulfonates

e.g. dishwashing liquids, shower gels, shampoo, etc.

Alkyl ether sulfates are milder to the skin than alkyl sulfates and generate less foam which is good for the formulation of laundry machine products

Cationic surfactants: Definition

Dissociate in aqueous solutions into:

- > amphiphilic cation (positively charged ion)
- halide anion (negatively charged halogen ion)
- They are widely used for treatment of synthetic fabrics and proteins molecules with negatively charged sites.
- Cationic surfactants are effective in acidic solutions and are not effective in alkaline solutions.

Cationic surfactants: Examples

Used as fabric softeners with anionic surfactant, helping them to break down the interface between the dirt/stain and the water.

$$CH_3$$
 CH_3 $CI^ CH_3$ $CI^ CI^ CH_3$ $CI^ CH_3$ $CI^ CH_3$ $CI^ CH_3$ $CI^ CI^ CH_3$ $CI^ CI^ CI^-$

Esterquats have ester linkage between the alkyl chains and the quaternary head-group makes them more biodegradable and less toxic

Non-ionic surfactants: Definition

<u>Do not dissociate</u> (do not form anions and cations) in aqueous solutions.

Do not bear an electrical charge and are often used together with anionic surfactants.

They are the second widely used after anionic surfactants; about 50% of surfactant production (excluding soap).

Non-ionic surfactants are insensitive to the water PH and hardness; do not interact with calcium and magnesium ions in hard water.

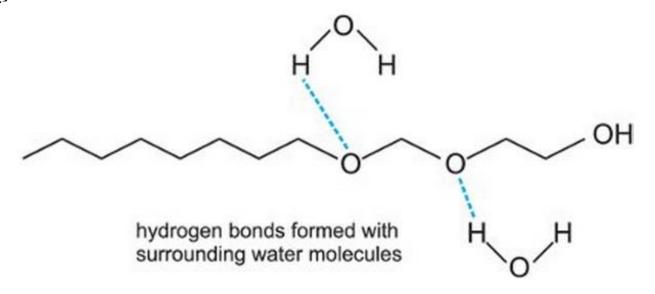
Non-ionic surfactants: Examples

Major group of nonionics are the ethoxylates made by condensing long chain alcohols with epoxyethane (ethylene oxide) to form ethers.

The long-chain alcohol can come from either a synthetic or natural source.

Non-ionic surfactants: Some hydrophilicity

Although they do not contain an ionic group as their hydrophilic component, hydrophilic properties are conferred by the presence of oxygen atoms in parts of the molecule which are capable of forming hydrogen bonds with molecules of water.



Non-ionic surfactants: Advantages

Nonionics are more surface active and better emulsifiers than anionics at similar concentrations.

Less soluble than anionics in hot water and produce less foam. They are also more efficient in removing oily and organic dirt than anionics.

Used in fabric washing detergents (both powders and liquids), in hard surface cleaners, and in many industrial processes such as emulsion polymerization and agrochemical formulations.

Amphoteric surfactants: Definition

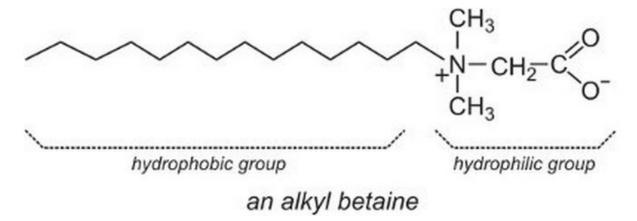
May be either anionic, cationic or no-ionic depending on the PH level of the aqueous solution.

A molecule of an amphoteric surfactant consists of a hydrophobic (lipophilic) tail and a hydrophilic portion having a properties of a zwitterion (a molecule with both positive and a negative electrical charge at different locations).

Bio-compatible and non-toxic, but very expensive!

Amphoteric surfactants: Examples

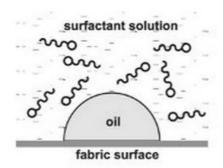
Almost all of contain a quaternary ammonium ion (cation). The negatively charged group can be carboxylate (-CO²⁻), sulfate (-OSO³⁻) or sulfonate (-SO³⁻). One such well-used class is the alkyl betaines which have a carboxyl group.



Betaines are neutral compounds with a cationic and an anionic group which are not adjacent to one another.

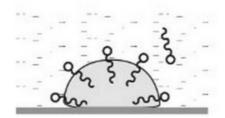
^{*}very mild and are used in shampoos and other cosmetics. They are said to be pH balanced

Surfactant applications

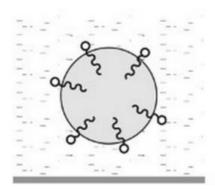


The surfactant contains molecules with hydrophilic and hydrophobic portions.

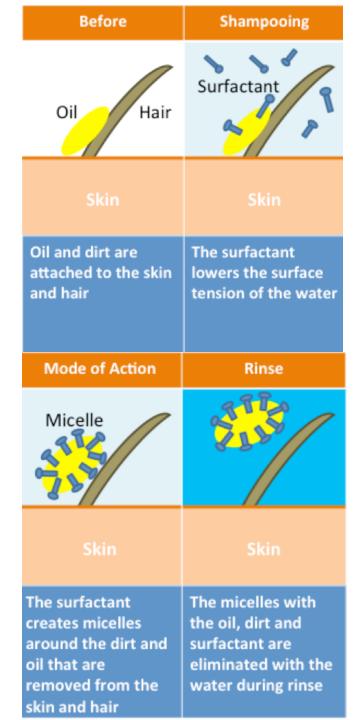
hydrophilic hydrophobic



Surfactant molecules are absorbed into the surface of the oil and so remove it from the fabric surface.



The surfactant molecules remain surrounding the oil once it has been removed, so helping to prevent its redeposition onto the cleaned surface.



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Washing up liquids

These formulations contain between 13-40% of surfactants which are predominantly alkyl ether sulfates (anionics) but also include nonionics and

amphoterics



Shampoos and shower gels

These tend to be based on alkyl ether sulfates and usually contain small amounts of other surfactants (most typically amphoterics) which help protect the skin from irritation and also condition the hair.







Hair conditioners / fabric softeners

These products are formulated using cationic surfactants



(sometimes combined with small amounts of non-ionic surfactants).

These are not cleansing products and the cationic surfactant is deposited onto the slightly negatively charged hair or cotton fibre surface, thus giving a lubrication benefit.

A typical detergent can contain up to 7 surfactants, 2 anionic, 3 non-ionic and 2 soaps.

Ingredient	Function
Sodium silicoaluminate	Builder
Sodium carbonate	Buffering agent
Sodium sulfate	Bulking agent
Sodium carbonate peroxide (sodium percarbonate)	Oxidizing agent
Sodium dodecylbenzenesulfonate	Surfactant
Water	Bulking agent
C12-15 pareth-5	Surfactant
Tetraacetyl ethylene diamine (TAED)	Bleach activator
Ceteareth-25	Surfactant
Citric acid	Builder
Sodium silicate	Builder
Sodium acrylic acid/MA co- polymer	Structurant

C12-15 pareth-7	Surfactant
Sodium stearate	Surfactant
Stearic acid	Surfactant
Tetrasodium etidronate	Sequestrant
Ethylenediaminetetra methylene phosphoric acid Ca/Na salt	Sequestrant
Maize starch	Bulking agent
Cellulose gum	Anti-redeposition agent
Parfum	Fragrance
Dimorpholinopyridazinone	Optical brightener
Sodium bentonite	Softness extender
Simethicone	Antifoaming agent
Sodium chloride	Bulking agent
Sodium polyacrylate	Structurant
Glyceryl stearate	Emulsifier
Sodium polyarylsulfonate	Surfactant

There are other ingredients, each with specific functions:

Bulking agents, (สารเติมเพิ่มปริมาณ) such as sodium sulfate and water.

Anti-caking agents, (สารต้านการแข็งตัว) e.g. aluminium silicate, which keep the powder dry and free-flowing.

Builders, usually sodium aluminosilicates, a type of zeolite, remove calcium and magnesium ions and prevent the loss of surfactant through scum formation.

Surfactants and the environment

In Western Europe all surfactant components of domestic detergents must be biodegradable.

This requirement resulted from the fact that the original alkylbenzene sulfonate anionics were based on branched alkenes and these proved resistant to degradation by bacteria at sewage treatment works causing many rivers to suffer from foam.

Industry has since moved (1980 onwards) to:

Linear alkylbenzene sulfonates and alcohol ethoxylates

Applications of surface and colloid chemistry

Food Emulsions (Milk Industry)

Ice cream consists of about 40% air frozen foam. The phases in foam consists of sugars, proteins, and emulsifiers. Typical ice cream contains:

Fats, 13%

Milk, 10%

Sugar, 16%

Emulsifier, 0.4%

Salts, 1%





Applications of surface and colloid chemistry

The air bubbles should remain dispersed, but as soon as it melts in the mouth (due to high temperatures), the emulsion should break.

This leads to the sensation of taste on the surface of tongue which is known to be related to the molecules' shape and physicochemical properties.







Applications of surface and colloid chemistry

Fire fighting, application of foams

Water is good enough for most cases, but a layer of foam (cause by surfactants) covers the flames and prevents contact with oxygen in the air.

Slower evaporation is good because volatile organics do not vaporize and "feed" the fire.



Summary of important concepts

What are the different type of colloids? How do they differ?

What is the EDL?

What is the DLVO theory?

What are micelles, how many types are there?

What is the critical micelle concentration?

Summary of important concepts

What are contact angles and how does that explain surface wetting?

How can we increase / decrease surface wetting in terms of surface energy and contact angles?

How many types of surfactants are there and how are they different?