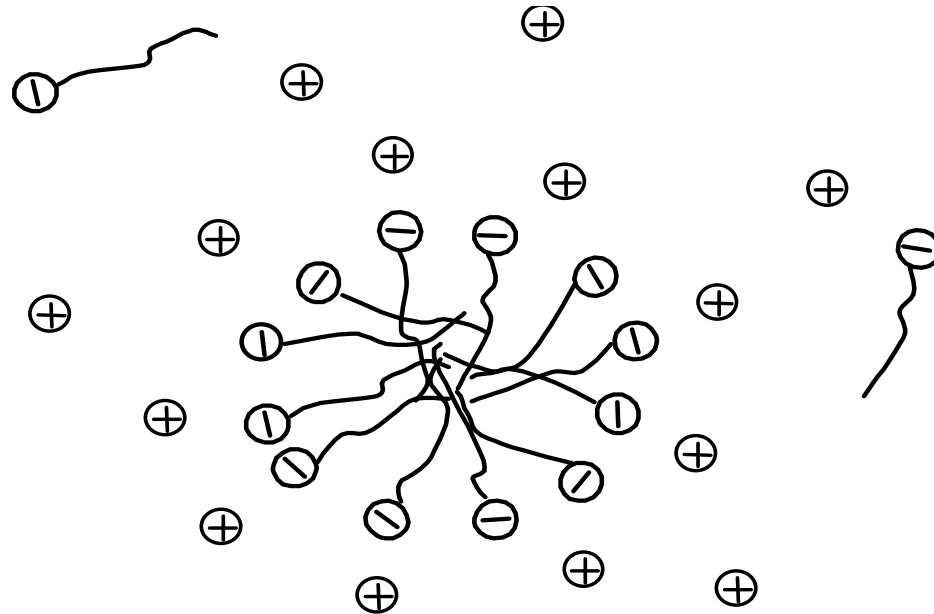


# MICELLES OF COLLOIDAL SURFACTANTS



# Formation of surfactant micelles in water: Driving forces

By definition, the dispersed systems are **lyophilic** if they are **thermodynamically stable**.

Hence, the dispersion of a solid or liquid sample of a colloidal surfactant in water with formation of micelles runs spontaneously:  $\Delta G_{disp} = \Delta H_{disp} - T\Delta S_{disp} < 0$ ,

and is reversible.

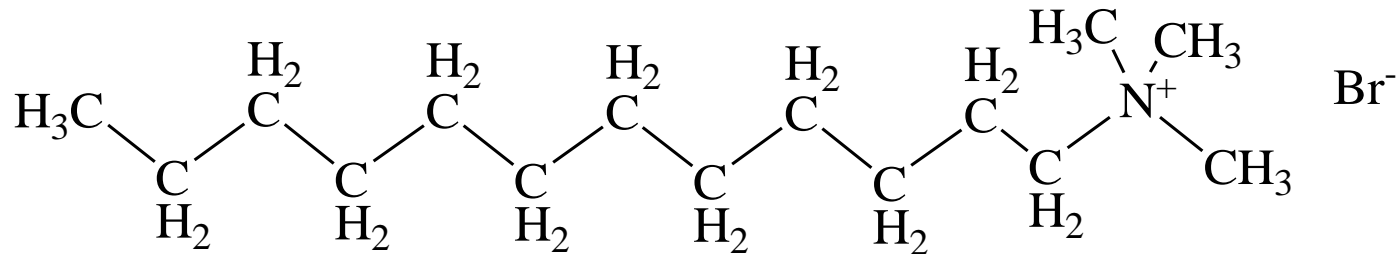
**Another criterion:** according to Reh binder -  
Shchukin

$$\pi d^2 \sigma \leq \beta k_B T$$

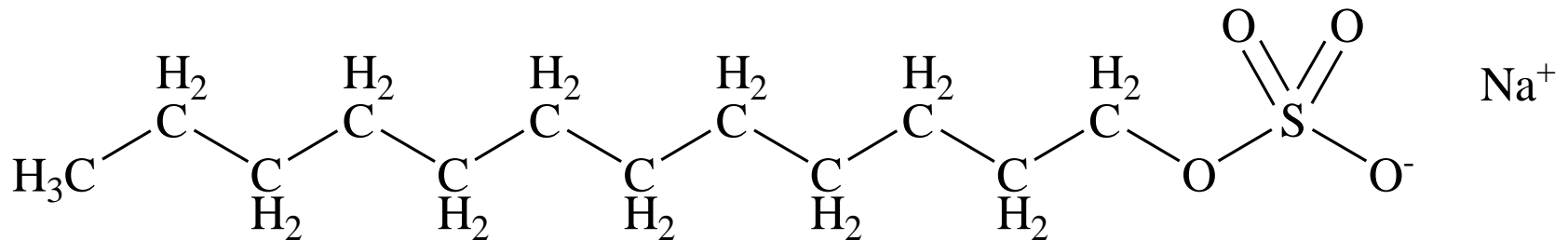
If the dispersed systems are thermodynamically stable, the excessive surface energy does not exceed the energy of the Brownian motion of water molecules.

For lyophilic systems, the micelle/water surface tension  $\sigma$  is about  $0.01 - 0.001 \text{ mJ m}^{-2}$

Typical colloidal surfactants consist of a hydrophobic hydrocarbon tail and a well-hydrated hydrophilic group. Therefore, they are called **amphiphilic** compounds:



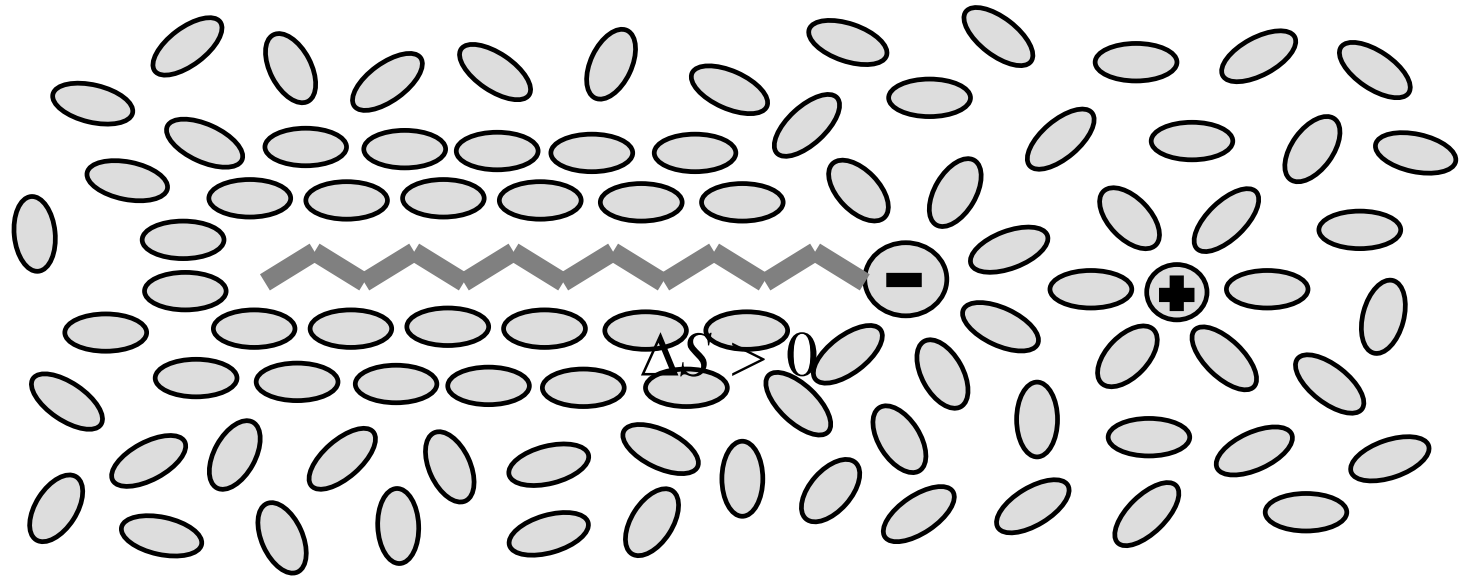
*n*-dodecyltrimethylammonium bromide



Sodium *n*-dodecylsulfate

(Br<sup>-</sup> and Na<sup>+</sup> are counter-ions)

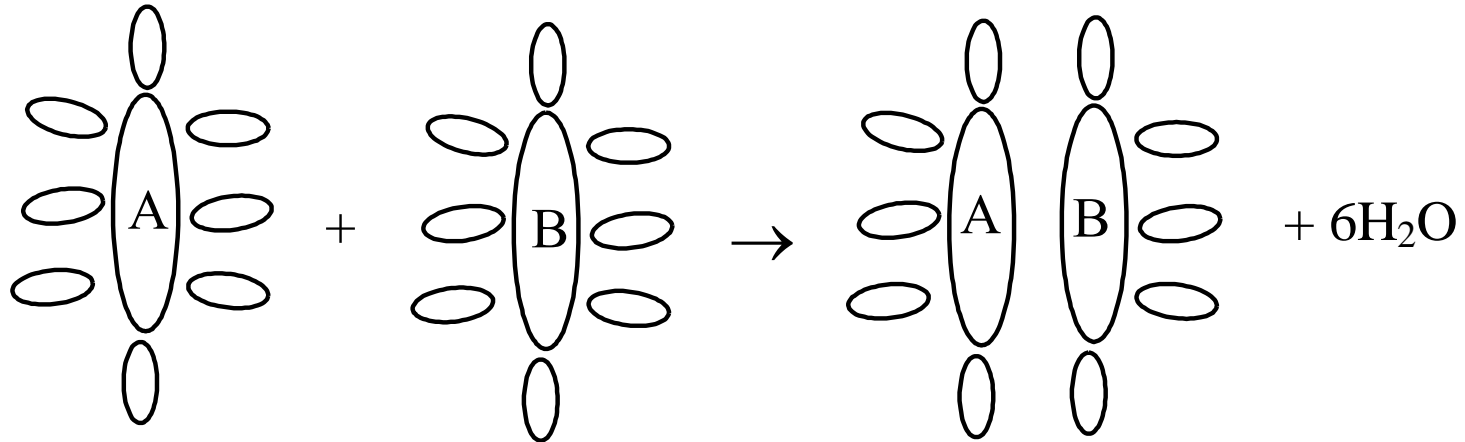
# Amphiphiles in water: hydrophobic hydration and micellization



Around the hydrophobic portion of a surfactant, the water becomes “ice-like”.

$\Delta S < 0$

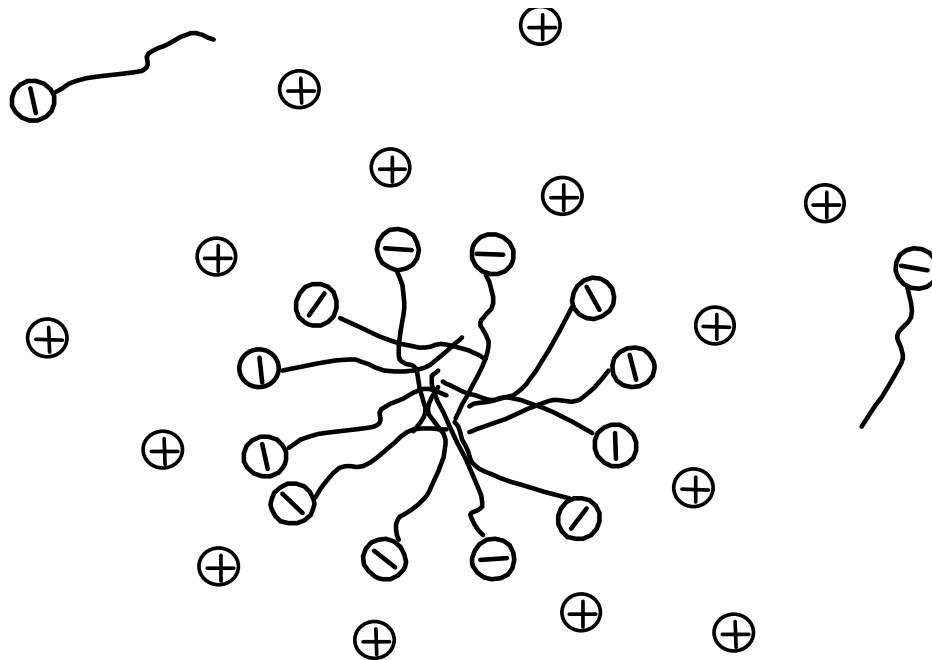
**Hydrophobic interaction** has an entropic nature:



water molecules are **released** from the ice-like shells:

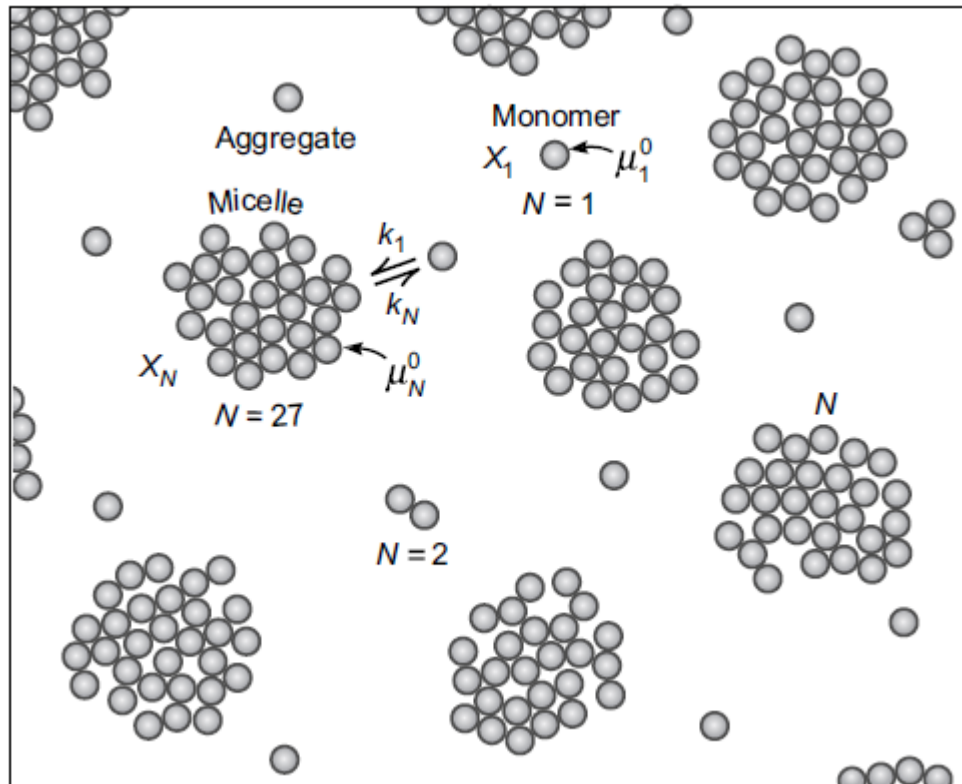
$$\Delta S > 0$$

Surfactant micelles are **dynamical systems**: some surfactant molecules leave the micelle, others come to their place; residence time of the monomer in micelle is  $10^{-5}$  to  $10^{-7}$  seconds.



In general, the micelle is "refreshed" in about 0.1-0.001 seconds

# A **dynamic equilibrium** between surfactant monomers and micelles in water



(From: J. N. Israelachvili, Intermolecular and surface forces, 2011)



Aggregation numbers of micelles,  $N_{aggr}$ , are usually on the order of **ten to the second power**.

According to the IUPAC definition:

“The surfactant concentration below which micelles are not detected by any physical methods is called the critical micelle concentration” = **CMC**

(критическая концентрация мицеллообразования, **ККМ**)

As a rule, the CMC are about 0.01-0.001 M or even lower.

For methods of determining this value, see textbooks on chemistry. There are over 100 methods described in the literature.

## **Micelles are strongly disordered highly hydrated clusters.**

Presently, they are widely used in biotechnologies, in High Performance Liquid Chromatography, in analytical and colloid chemistry, etc.

There are two main approaches to describe the process of micelle formation: (i) pseudophase model; (ii) quasi-chemical model.

Both are ca. equal and give a similar result.

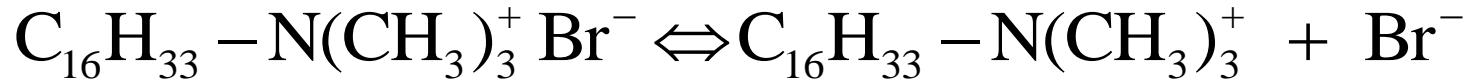


$$\frac{N}{N_A} = K_{mic} \cdot (x_{surf})^{N_{aggr}}$$

Here  $N$  stands for the number of micelles per unit volume,  $K_{mic}$  is the equilibrium constant of micellization, is  $x_{surf}$  the surfactant monomers equilibrium concentration in the bulk water.

## Peculiarity of ionic surfactants: electrolytic dissociation

In monomeric state: complete dissociation



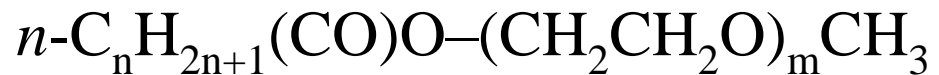
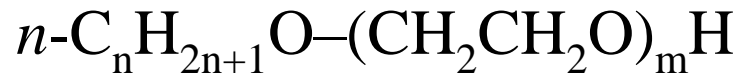
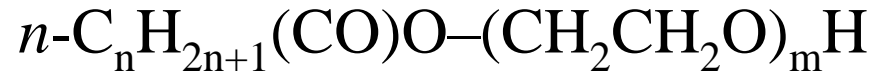
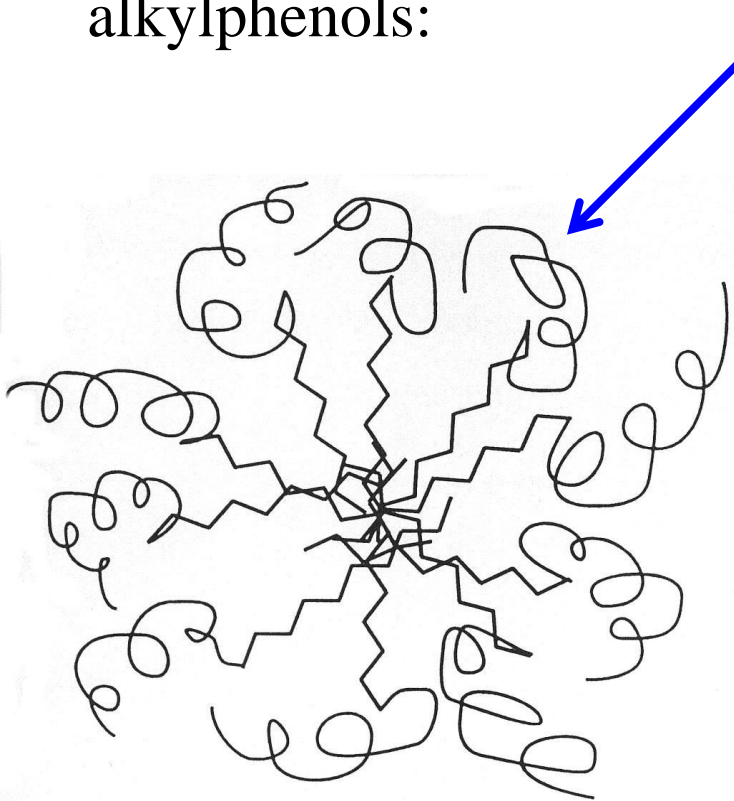
In micelles: incomplete dissociation



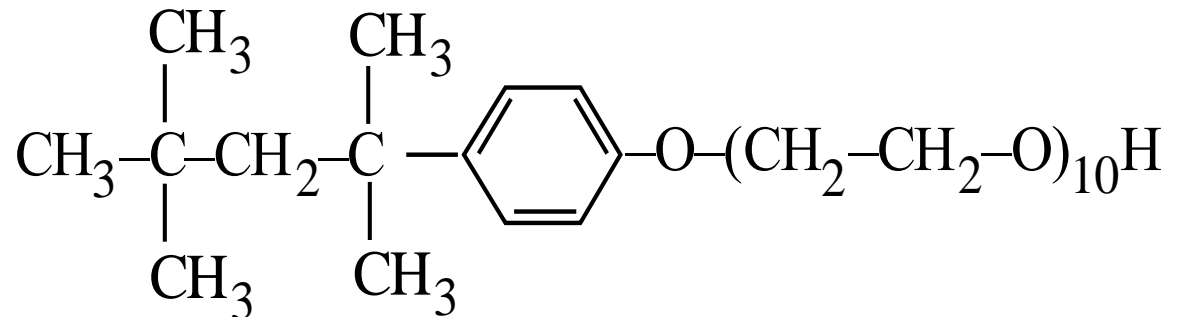
$\beta = \frac{m}{n}$ ; normally,  $\beta$  is within the range of 0.6-0.9



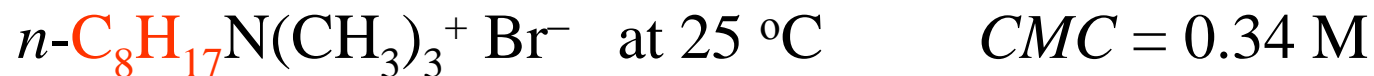
**Nonionic surfactants:** oxyethylated long-tailed acids, alcohols, or alkylphenols:



Triton X-100:



## Dependence of the *CMC* on the tail length:



$$\log (\text{CMC}) = A - Bn$$

(similar to the Traube rule for the surface activity)

## Role of the counter-ion:



## Structure and CMC

Surfactant	CMC, M	t °C
$C_{12}H_{25}COO^-K^+$	0.0125	25
$C_{12}H_{25}COO^-Na^+$	0.0117	40
$C_{12}H_{25}OSO_3^-Na^+$	0.0083	25
$C_{12}H_{25}OSO_3^-K^+$	0.008	
$C_{12}H_{25}OSO_3^-Li^+$	0.009	25
$(C_{12}H_{25}OSO_3^-)_2Mg^{2+}$	0.00125	30
$C_{12}H_{25}SO_3^-Na^+$	0.009	20
$C_{12}H_{25}-(C_6H_4)-SO_3^-Na^+$	0.0012	60
$C_{12}H_{25}NH_3^+Cl^-$	0.014	30
$C_{12}H_{25}N(CH_3)_3^+Cl^-$	0.016	30
$C_{12}H_{25}N(CH_3)_3^+Br^-$	0.0144	25
$C_{12}H_{25}N(C_4H_9)_3^+Br^-$	0.0048	25
$C_{12}H_{25}N(CH_3)_3^+ C_{12}H_{25}OSO_3^-$	0.00003	25
$C_{12}H_{25}-\overset{+}{N} \begin{array}{l} \diagup \\ \diagdown \end{array} -Cl^-$	0.016	25
$C_{12}H_{25}NC_5H_5^+Br^-$	0.014	25
$C_{12}H_{25}NC_5H_5^+I^-$	0.0045	30
$C_{12}H_{25}-NH-C_2H_4-COO^-K^+$	0.0026	35
$C_{12}H_{25}O(CH_2CH_2O)_{23}H$	0.000062	25
$C_{12}H_{25}OPO_3^{2-}(Na^+)_2$	0.057	25
$(C_{12}H_{25})_2N(CH_3)_2^+Cl^-$	0.00018	25

# Thermodynamics of micellization

$$\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic}$$

$$\Delta G_{mic} = RT \ln(CMC)$$

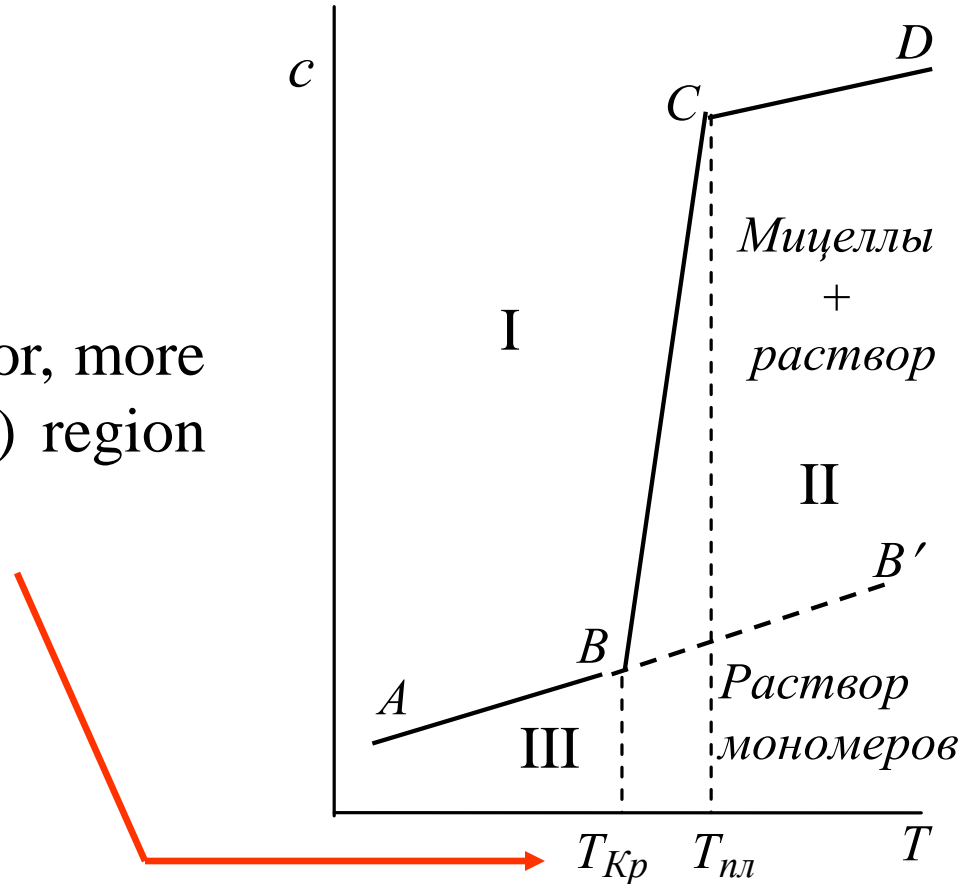
Van't Hoff equation:

$$\Delta H_{mic} = -2,303RT_{mic}^2 \frac{d(\log CMC)}{dT}$$



F. Krafft (1895)

*The Krafft point ( $T_{Kr}$ ), or, more correct, Krafft (narrow) region of temperatures*



Dependence of ionic surfactants' solubility in water on temperature

The Gibbs phase rule:

$$f = K - \Phi + 2 \text{ или } f = K - \Phi + 3 \text{ ?}$$



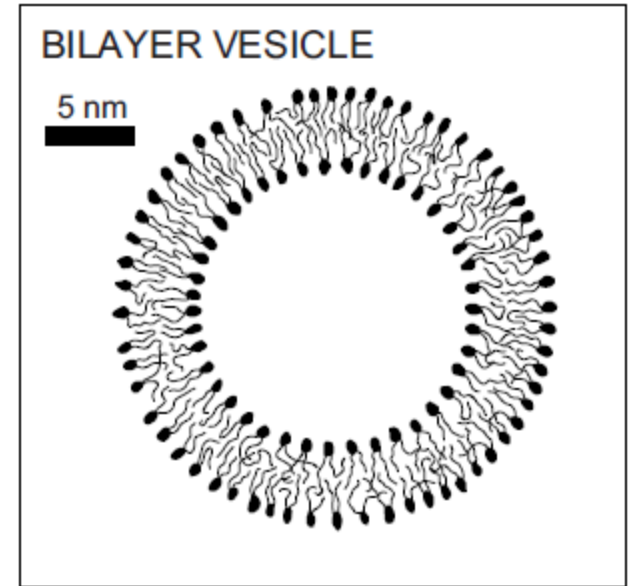
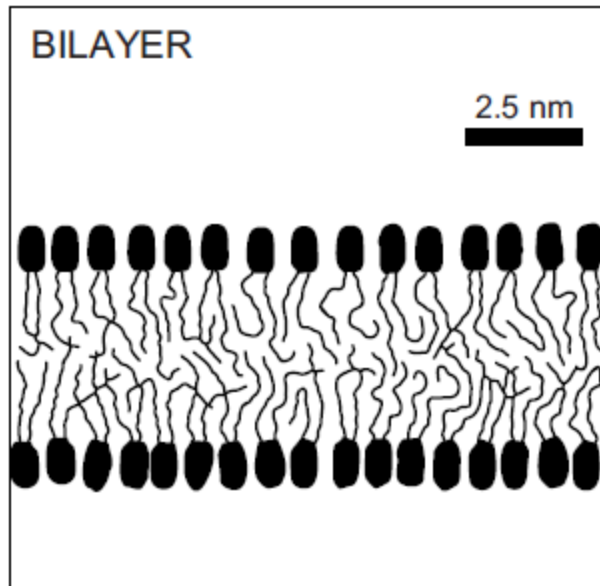
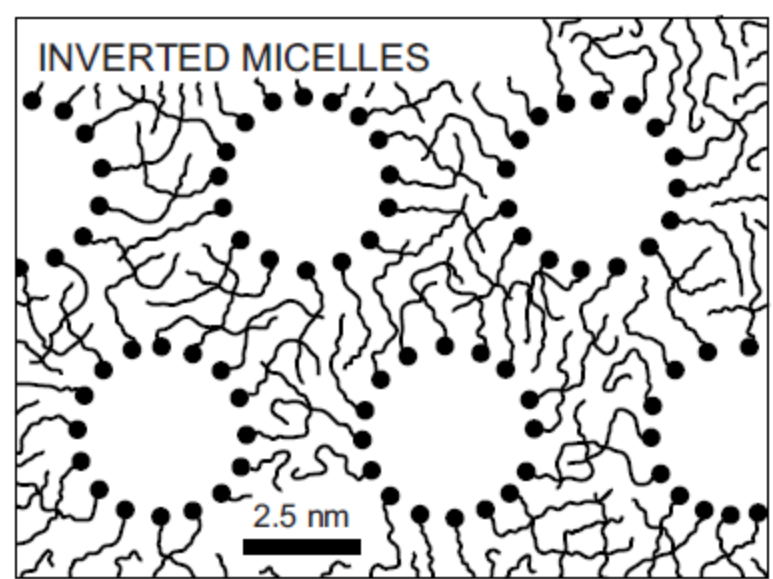
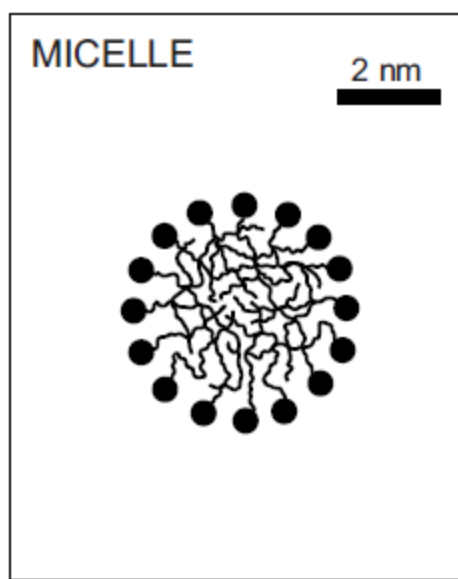
**Explanation:** at lower temperatures, the water structure is similar to that of ice, and the entropic factor can no longer ensure the formation of micelles of an ionic surfactant.

The  $T_{Kr}$  value depends on the tail length and the nature of the ionic group.

**For non-ionic surfactants**, there is only an upper temperature limit: cloud point.

The hydration of the oxyethylene groups decreases along with the temperature increase, and the system becomes thermodynamically unstable.

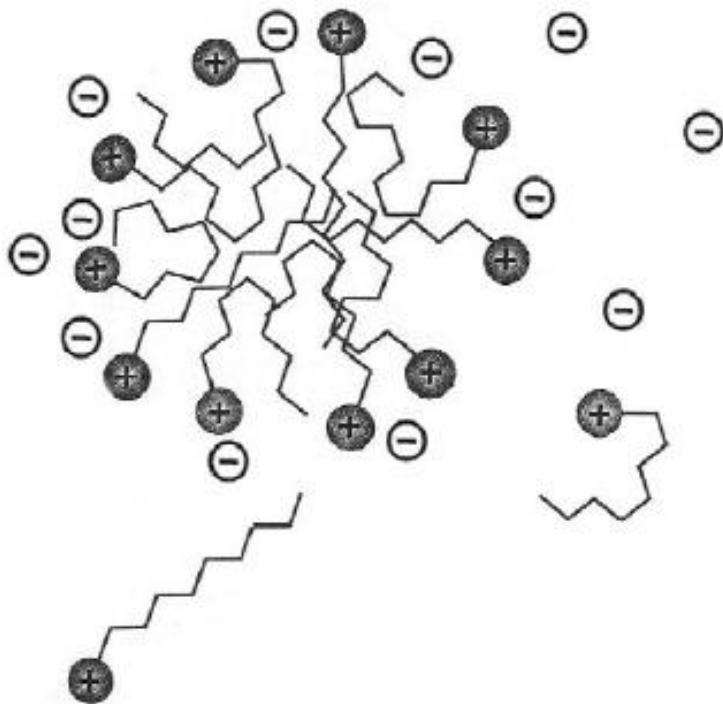
Related systems



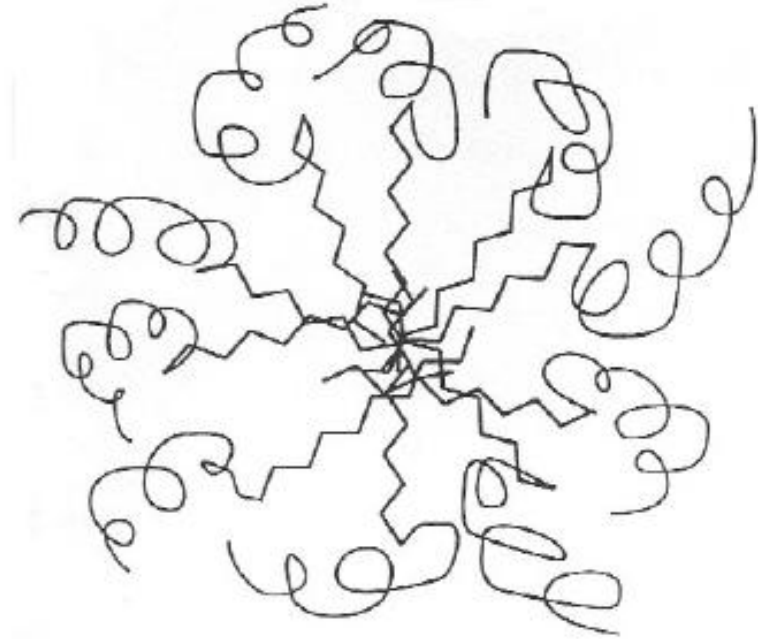
(From J. N. Israelachvili, Intermolecular and surface forces, 2011)



# Structure and some properties of surfactant micelles in water



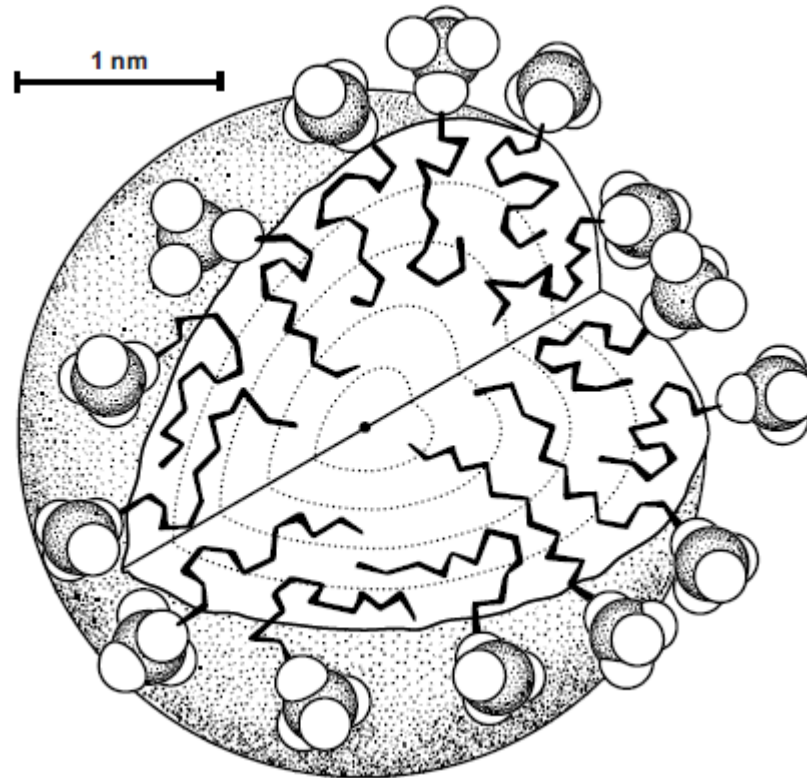
**A**



**B**

A schematic sketch of the section of cationic (A) and nonionic (B) surfactant micelles.

# Sodium *n*-dodecylsulfate micelle in water



(From J. N. Israelachvili, Intermolecular and surface forces, 2011)

According to Tanford, the length of the hydrocarbon chain is:

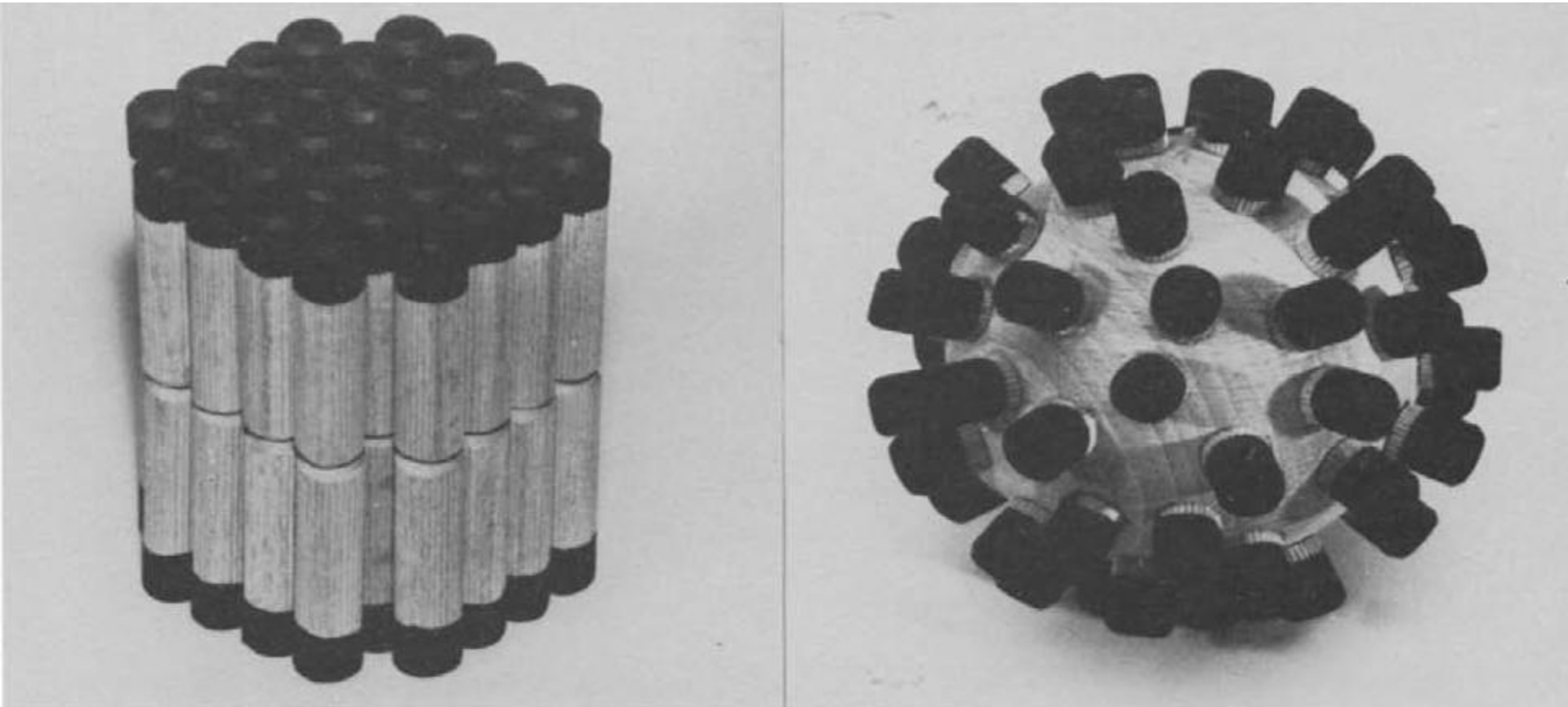
$$l = 0.154 + 0.1265n \text{ (nm)},$$

where  $n$  is the number of C atoms.

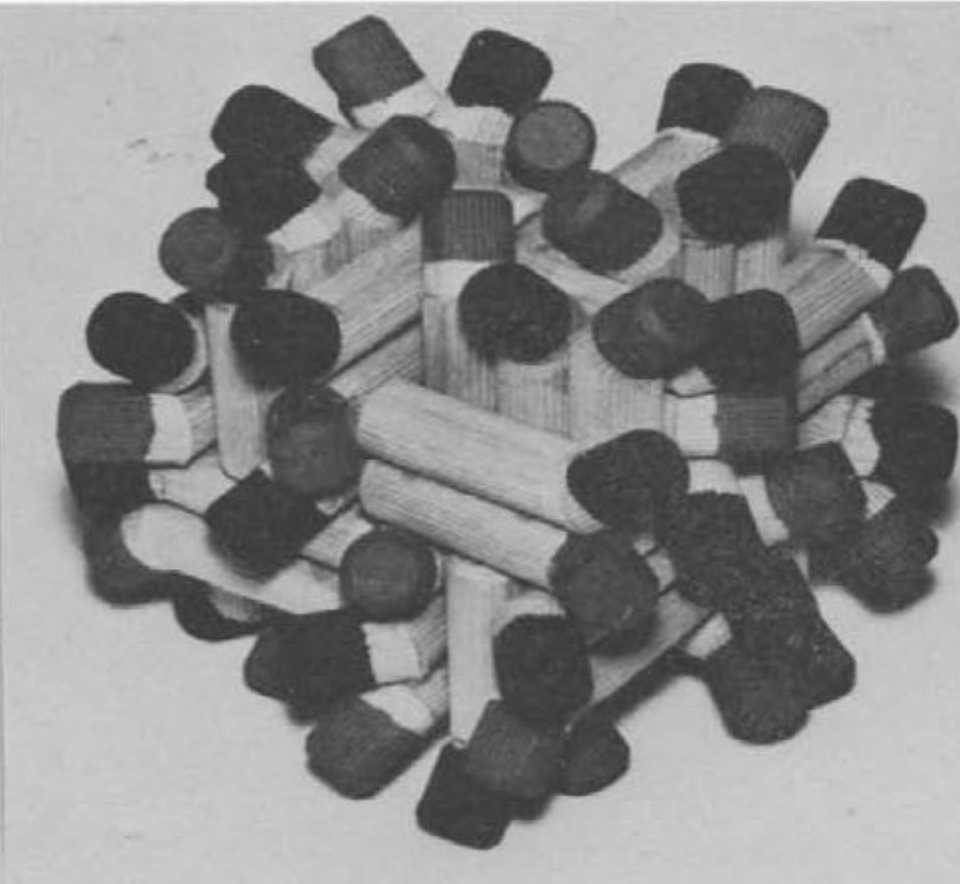
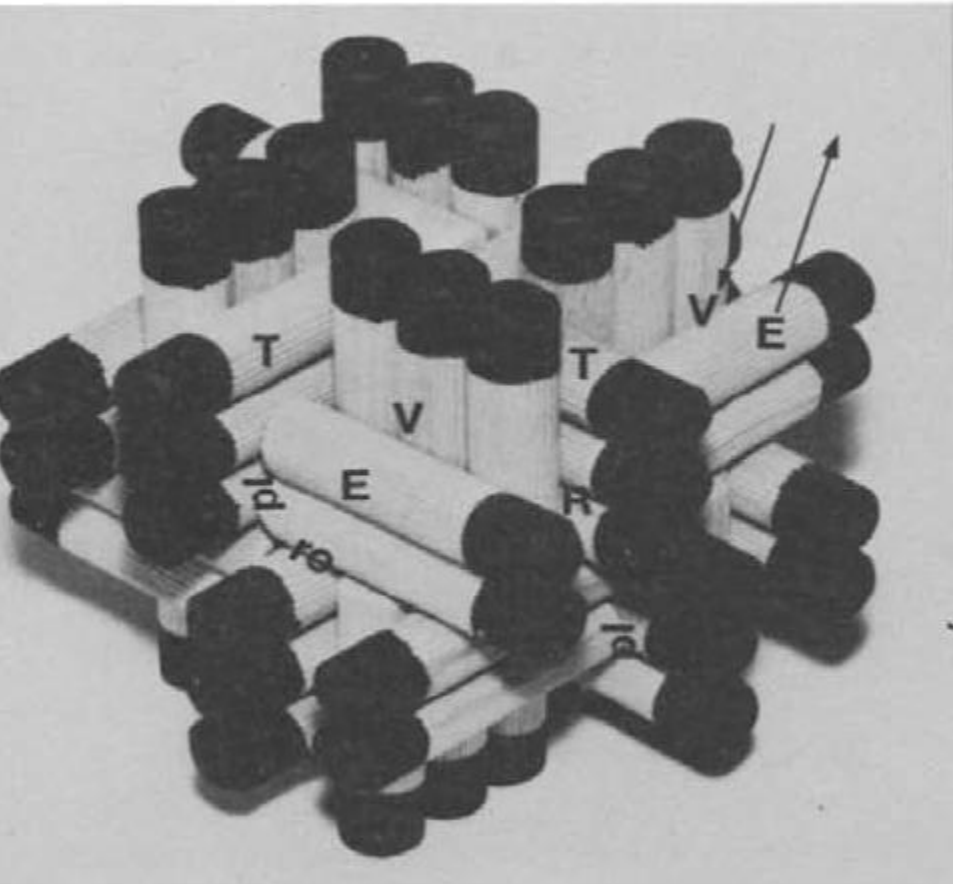
Sodium  $n$ -dodecylsulfate spherical micelle:

$$\text{radius of the hydrocarbon core} = l = 0.154 + 0.1265 \times 12 = 1.67 \text{ nm}$$

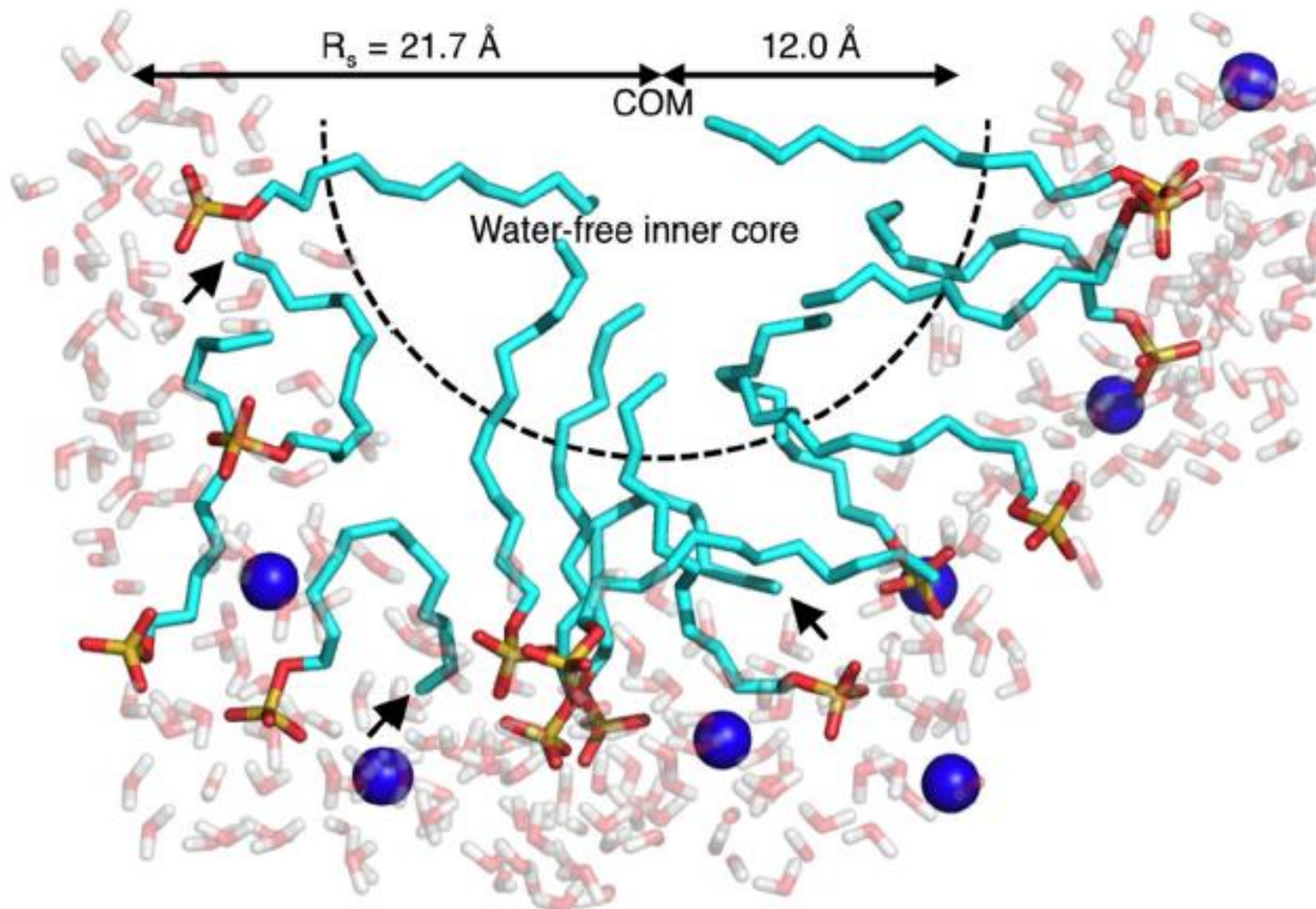




McBain (left) and Hartley (right) models of micelles



Fromherz models; water penetration depth ?!!



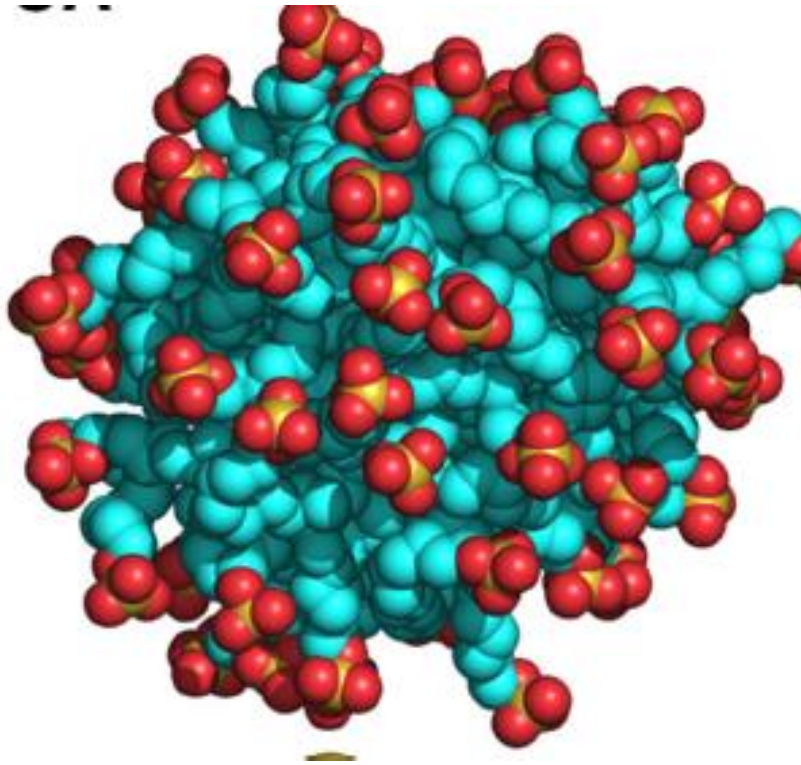
J Mol Model (2014) 20:2469  
DOI 10.1007/s00894-014-2469-0

ORIGINAL PAPER

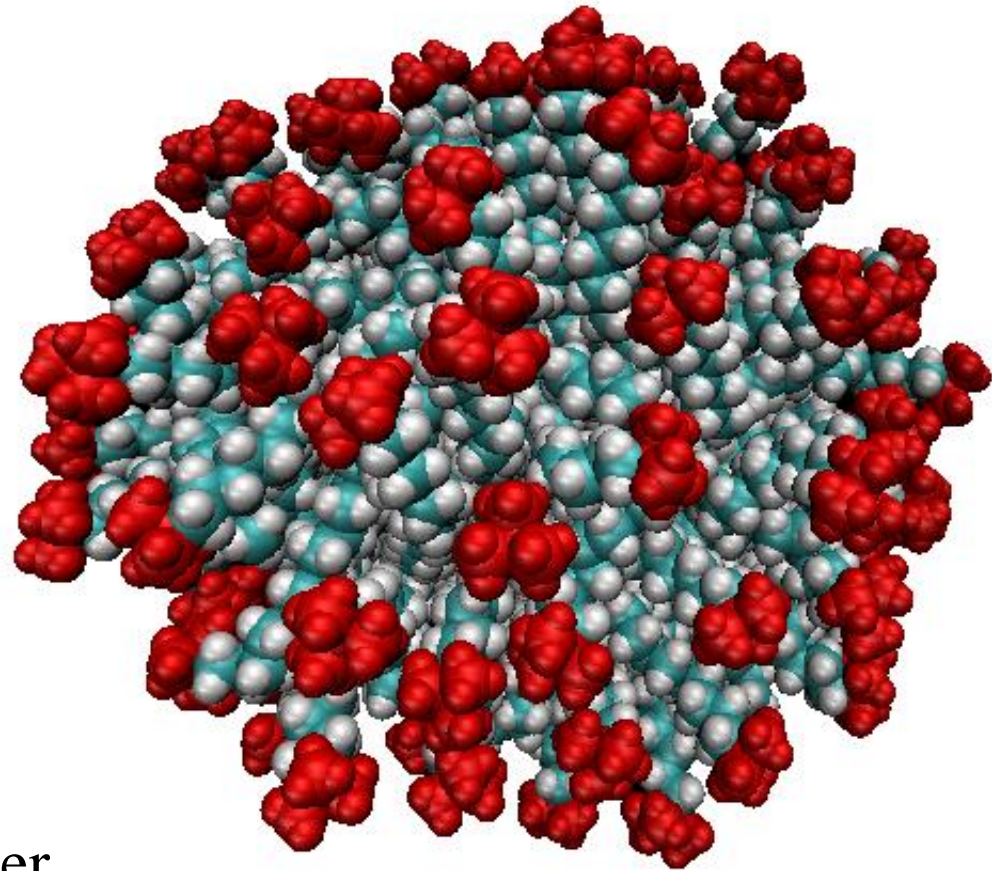
## Multiscale molecular dynamics simulations of sodium dodecyl sulfate micelles: from coarse-grained to all-atom resolution

Guillaume Roussel · Catherine Michaux ·  
Eric A. Perpète

## Molecular dynamics simulation



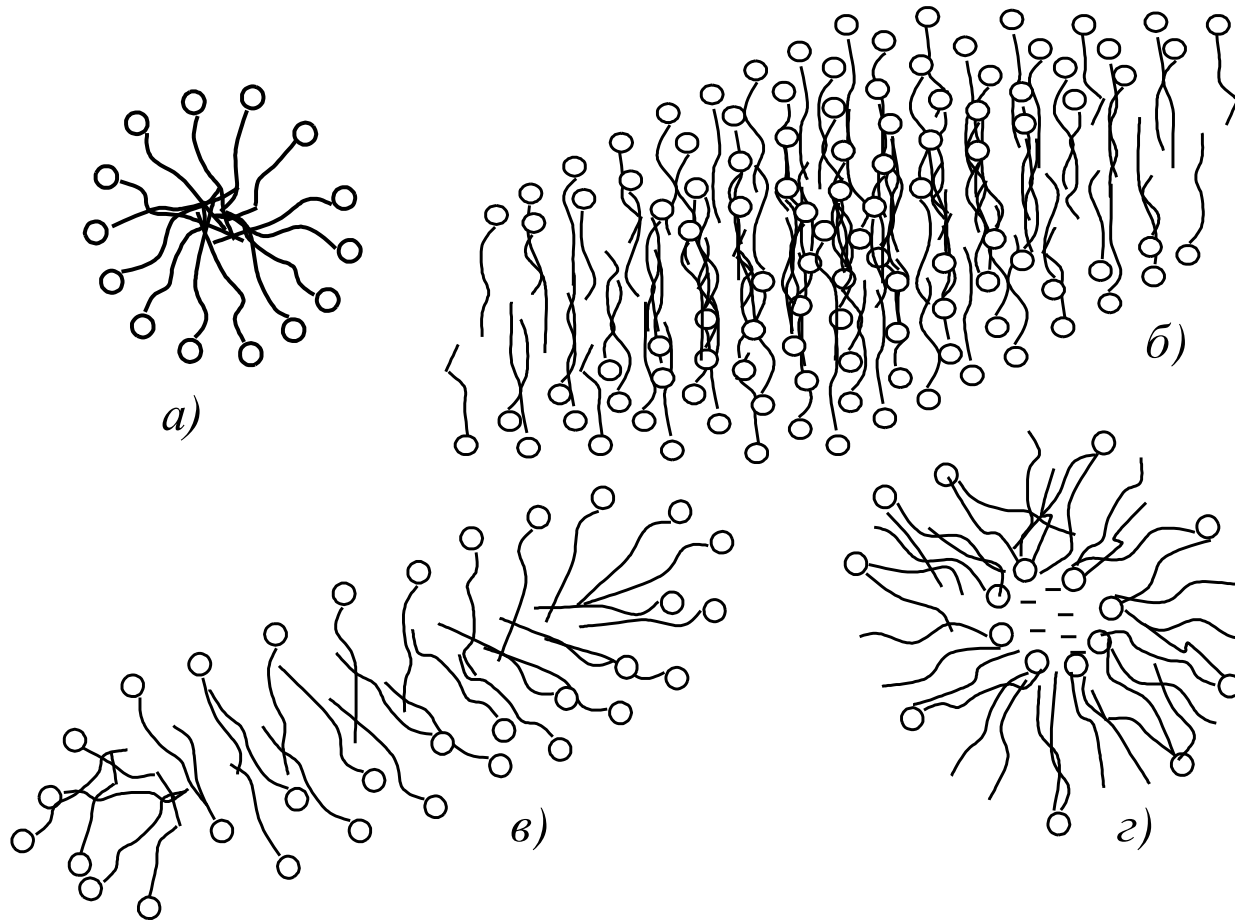
Sodium *n*-dodecylsulfate in water



Cetyltrimethylammonium  
bromide micelles in water

(V. S. Farafonov, A. V. Lebed, 2017)

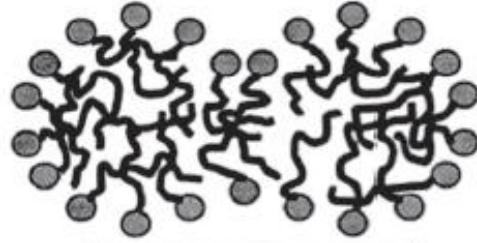
# Polymorphism of surfactant micelles



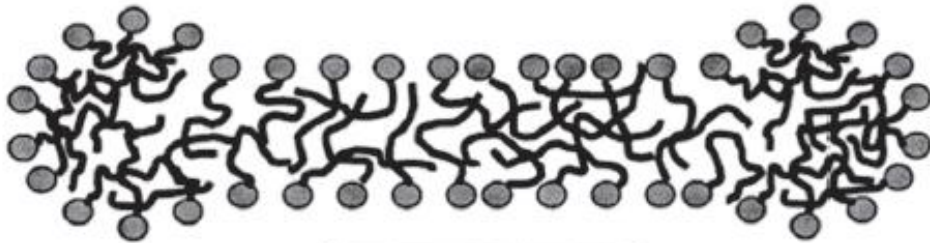
Micellar structures by Hartley (a), McBain (б), Debye (в), and reversed micelle or water-in-oil microemulsion (г)



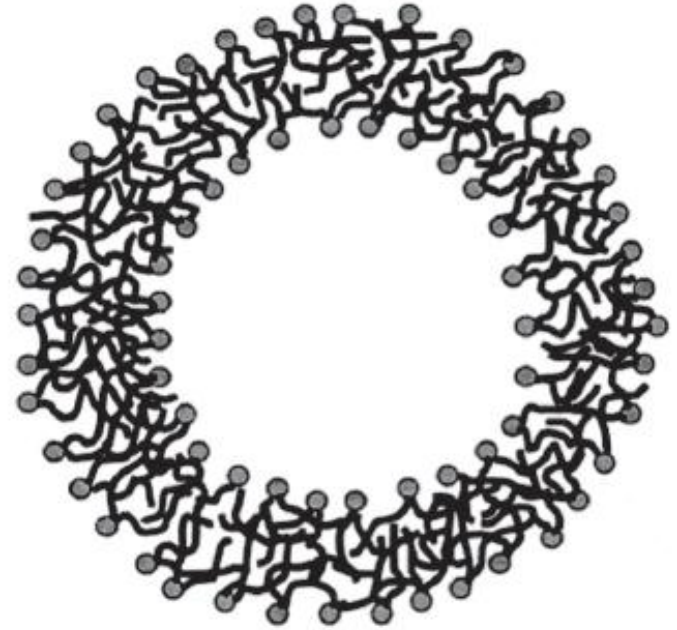
Spherical micelle



Globular micelle



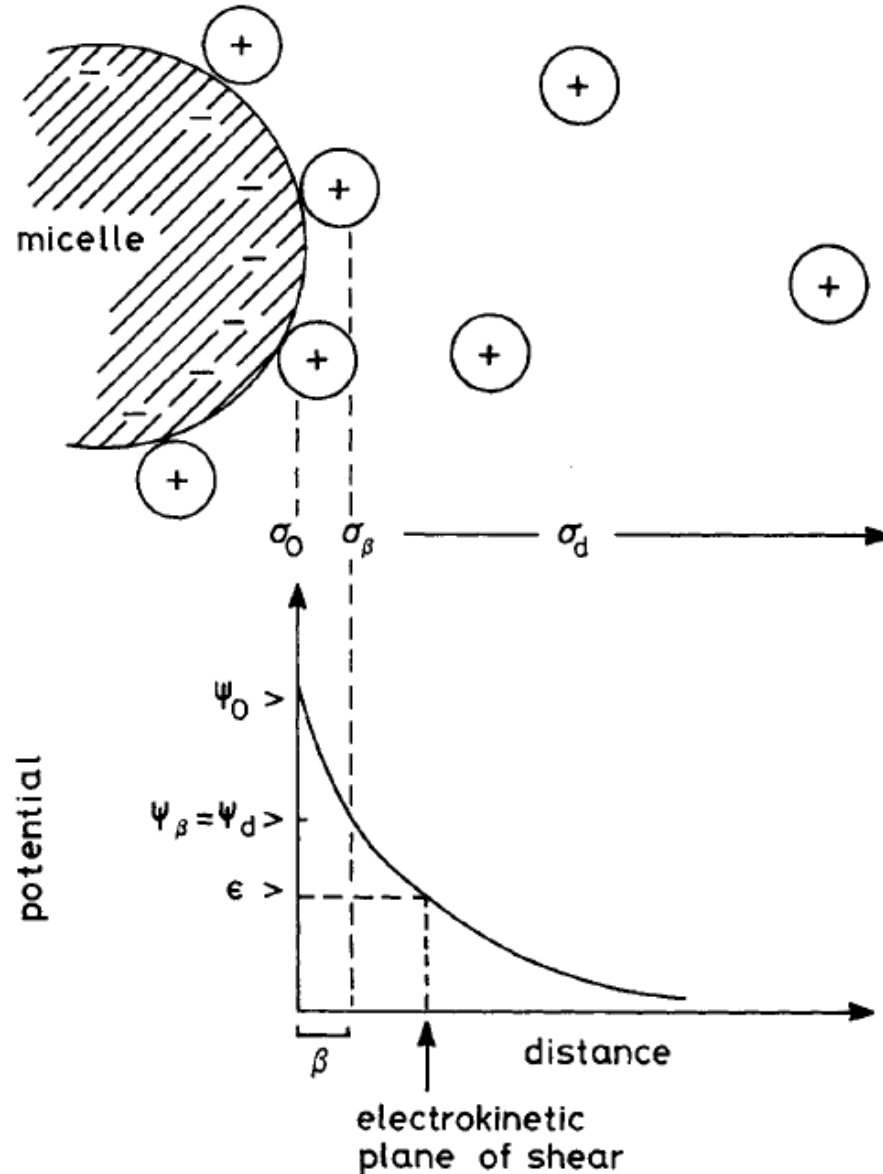
Rodlike micelle



Spherical bilayer vesicle

(R. Nagarajan, 2014)

# Double electrical layer on the micellar surface



(Hartland, Grieser, White)

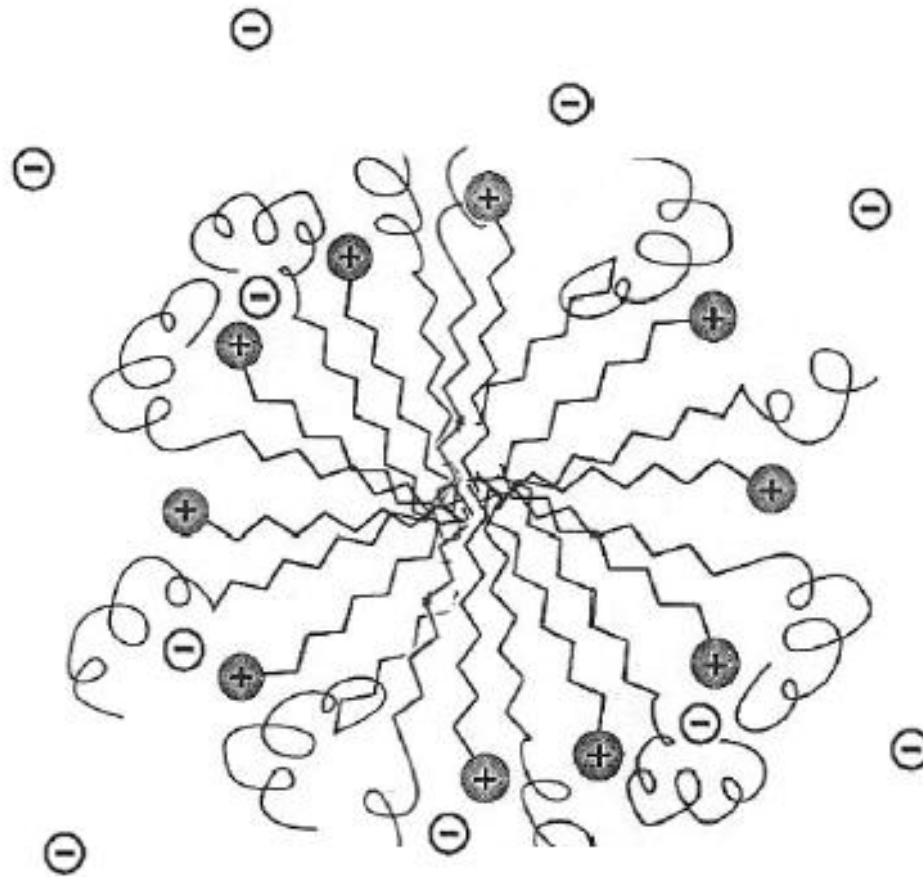
## Ohshima, Healy, White equation for a spherical charged colloidal particle

$$\frac{\alpha}{s_i} - \frac{2\varepsilon\varepsilon_o kRT}{F} \sinh(Y / 2) \left( 1 + \frac{2}{kr \cosh^2(Y / 4)} + \frac{8 \ln [\cosh(Y / 4)]}{(kr)^2 \sinh^2(Y / 2)} \right)^{\frac{1}{2}} = 0$$

Here,  $s_i$  is the area of the charged head-group,  $Y = \Psi F / RT$ ,  $F$  is the Faraday constant,  $k^{-1}$  is the Debye length,  $\varepsilon_o = 8.854 \times 10^{-12} \text{ F m}^{-1}$ ,  $\varepsilon = 78.5$  at  $T = 298.15 \text{ K}$ . Actually,  $\alpha/s_i$  is the surface charge density.

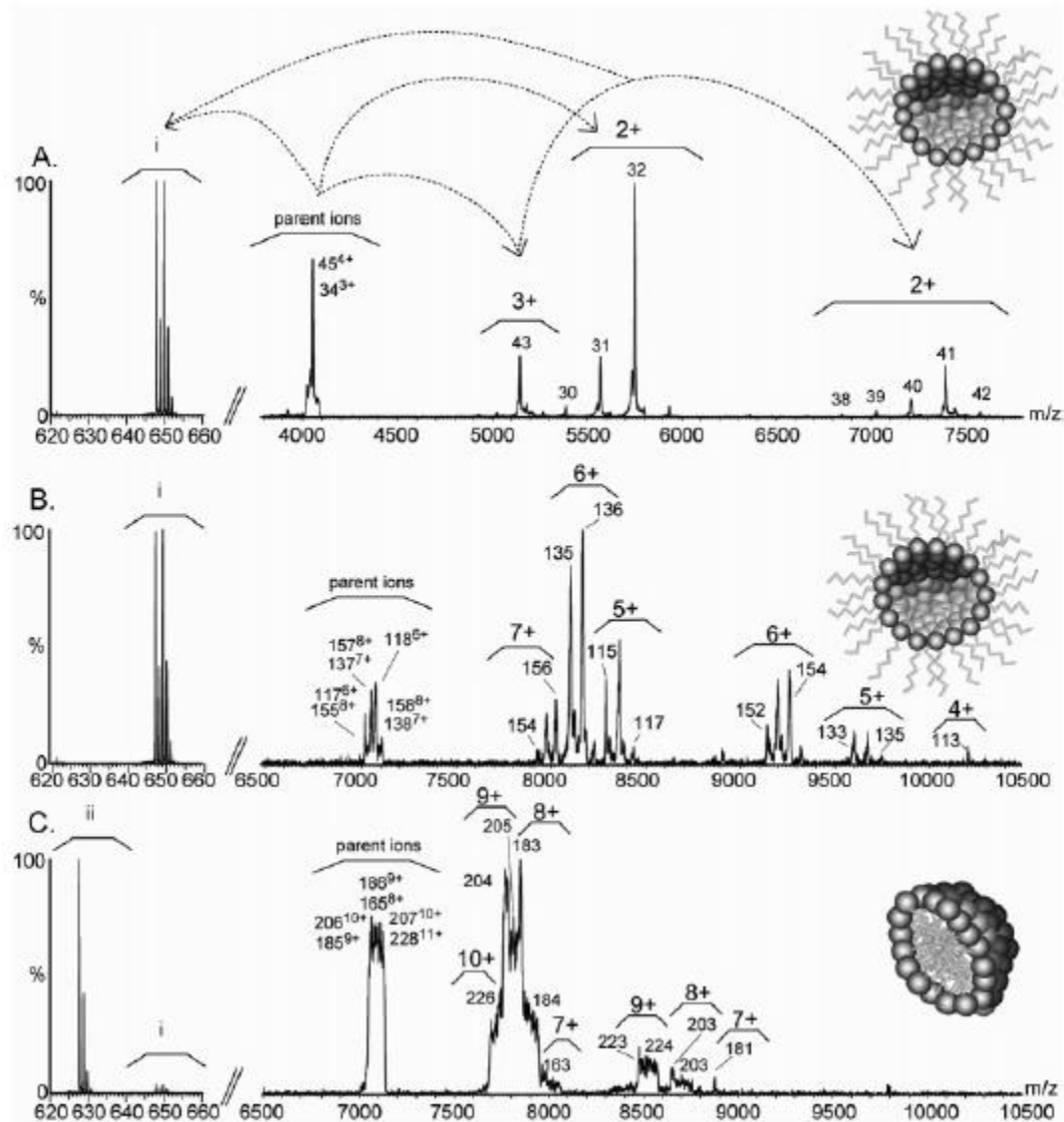


## Mixed surfactant micelles



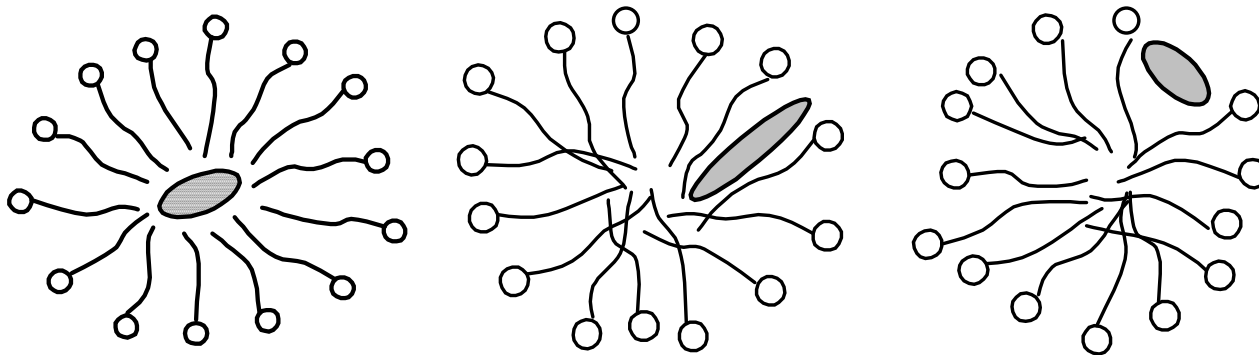
A schematic sketch of the section of a spherical (cationic + nonionic) mixed surfactant micelle

# Micelles in the gas phase

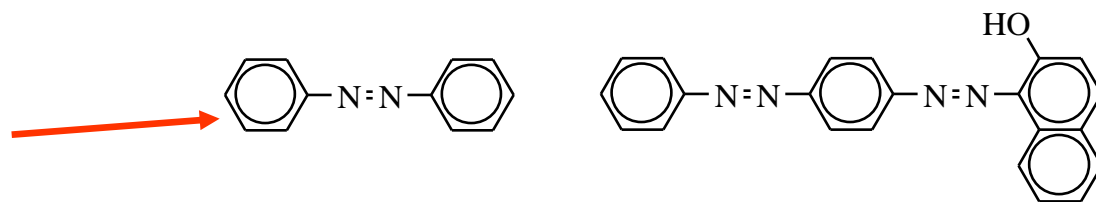


(Electrospray mass spectrometry, Sharon et al., 2006)

# Solubilization: colloidal solubility of water-insoluble compounds and binding of water-soluble species

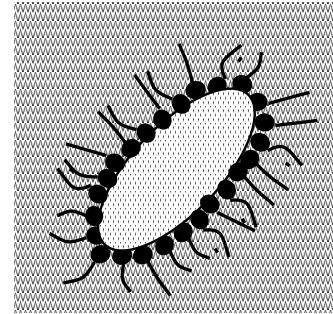
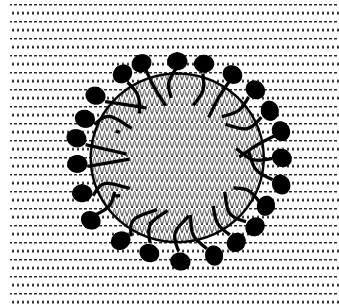


Azobenzene and Sudan III



Difference between solubilization and dispersion

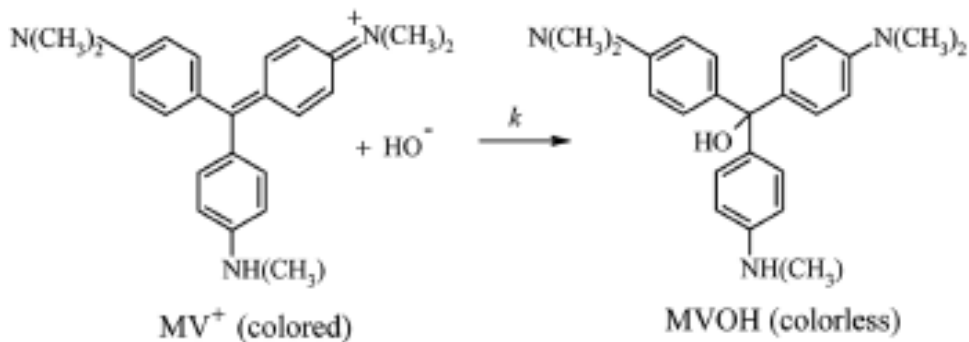
# Stabilization of lyophobic colloidal particles by surfactants



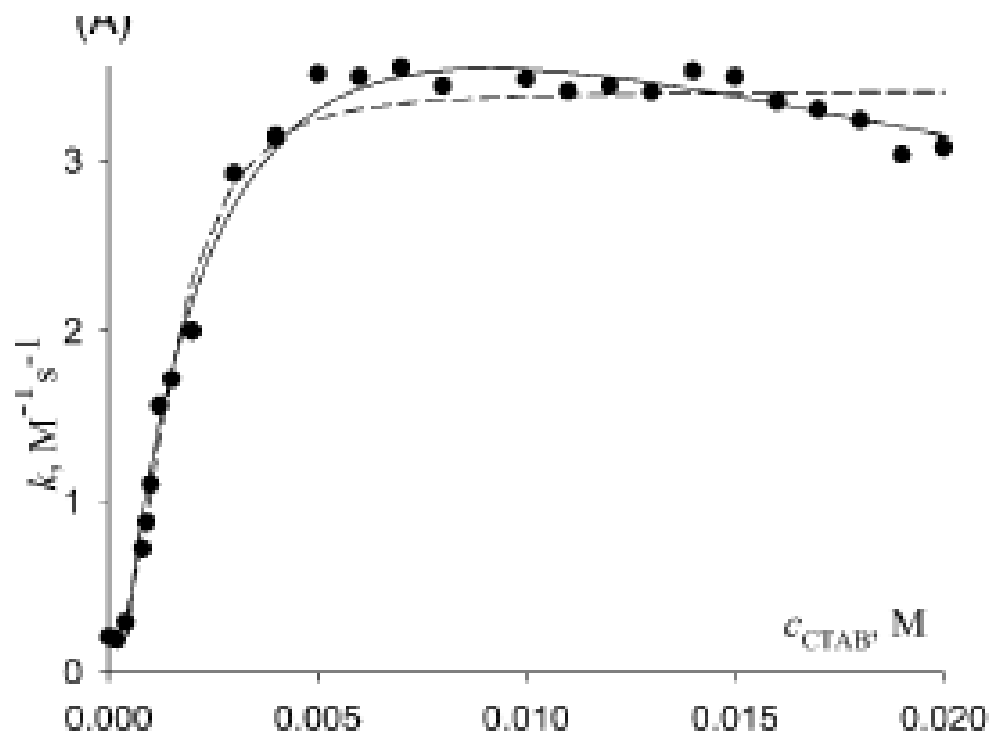
A particle of an oil-in-water microemulsion and a particle of suspension in oil

(here, oil means a non-polar solvent, such as heptane, benzene, etc.)

# Micellar catalysis



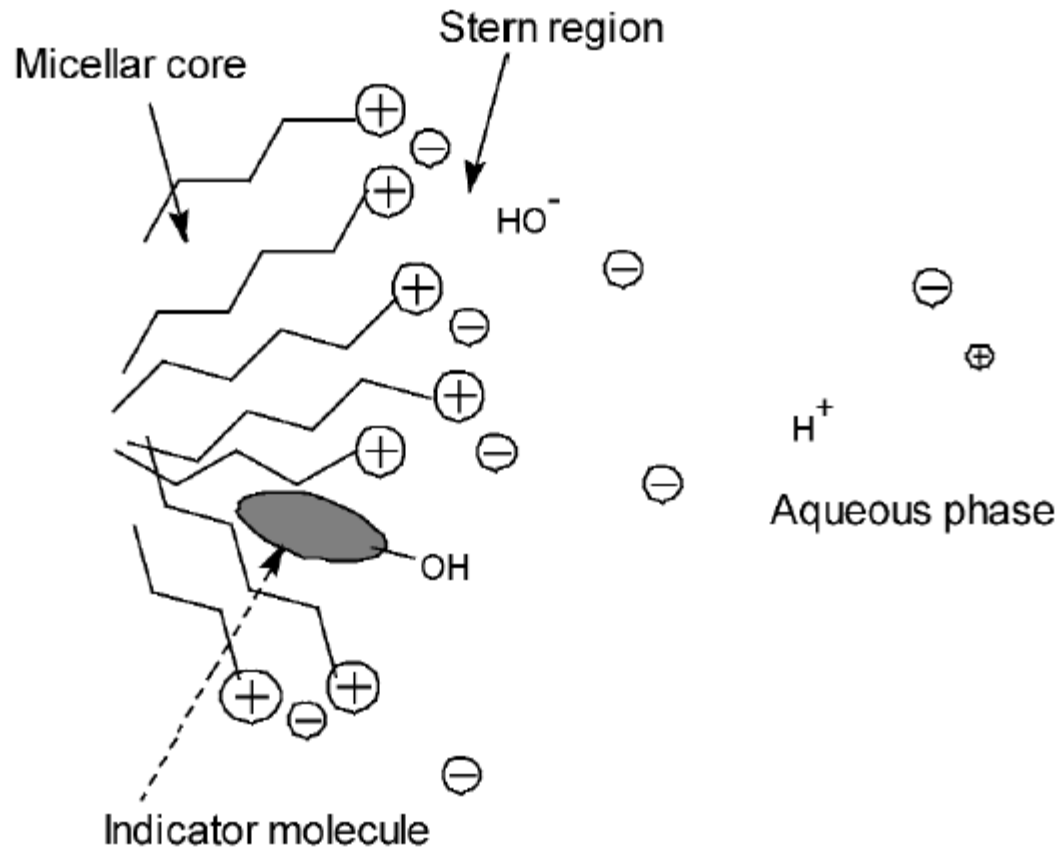
Reaction rate 



Laguta, Eltsov, 2019

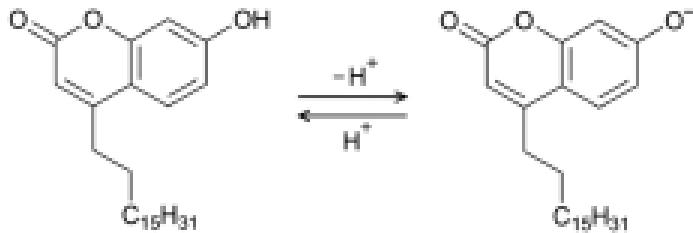
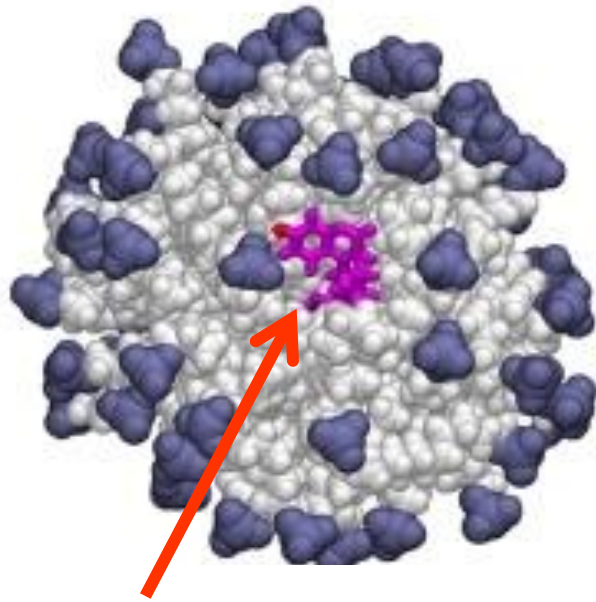
Surfactant concentration

# Examining of surfactant micelles using indicators

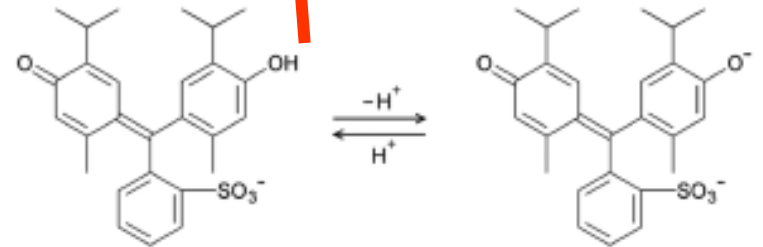
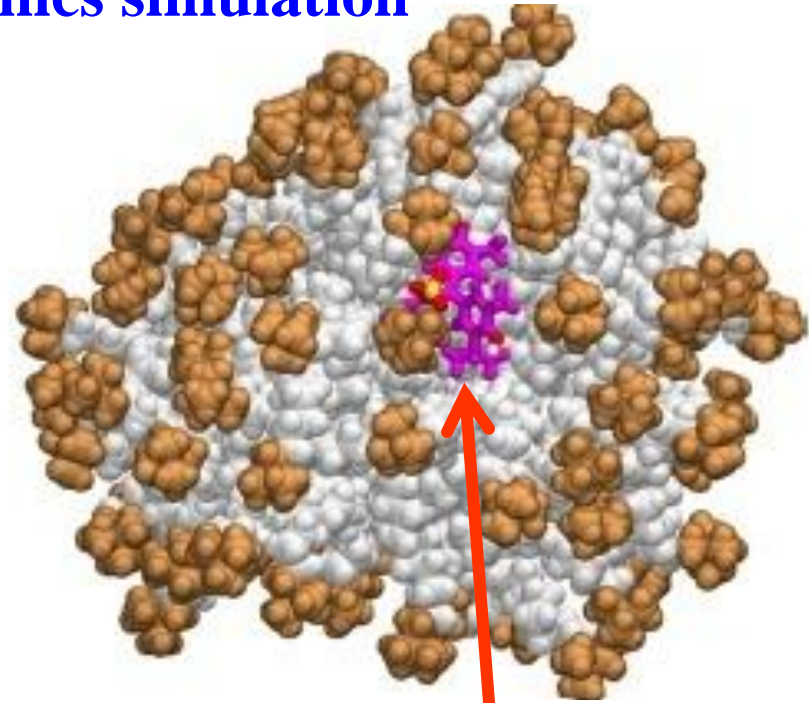


A schematic picture of a fragment of a cationic micelle with an embedded indicator.

## Molecular dynamics simulation



In sodium *n*-dodecylsulfate  
micelle



In cetyltrimethylammonium  
bromide micelle

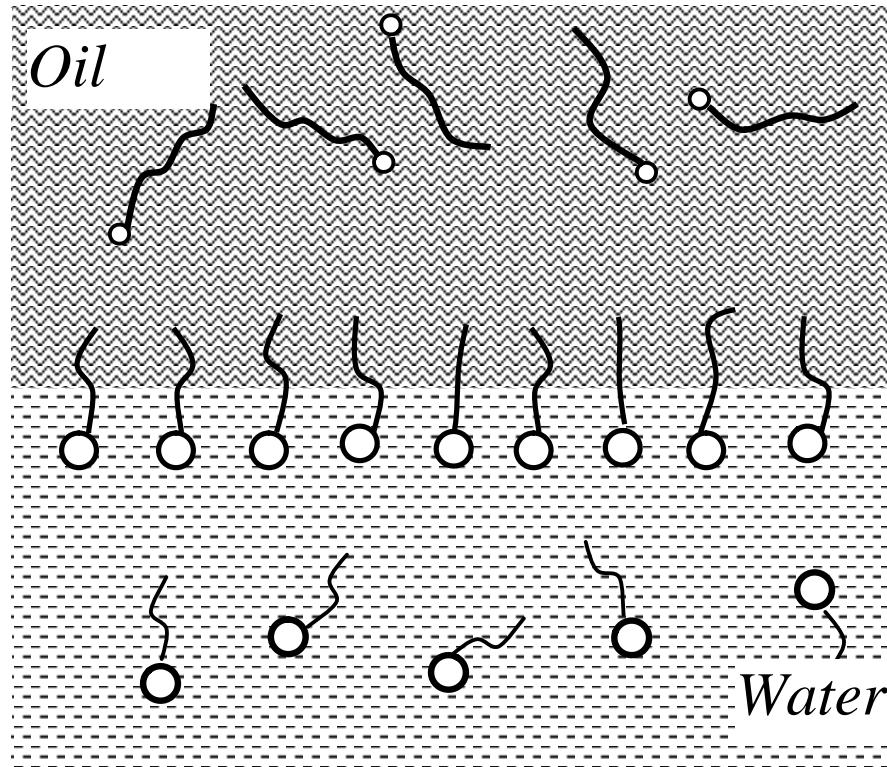
(Farafonov, 2020)





# Гидрофильно-гидрофобный (иначе гидрофильно-олеофильный, или гидрофильно-липофильный) баланс. Числа ГЛБ

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Гидрофильно-липофильный баланс: ГЛБ смещен в сторону гидрофильности (а); липофильности (в); оптимальный вариант (б)

# Моющее действие коллоидных ПАВ

1. Хорошее смачивание их поверхностей моющей жидкостью, и, в частности, проникновение воды в тонкие капилляры. Это достигается снижением поверхностного натяжения воды при добавке ПАВ.

2. Молекулы (ионы) мыла, адсорбируясь на поверхности волокна и на твердых и жидких частицах загрязнений, формируют хорошо гидратированный адсорбционный слой. Это создает предпосылки для отрыва от поверхности волокна частиц загрязнений и последующего их дробления. При этом избирательное смачивание волокон ткани приводит к “отталкиванию” масляных загрязнений с очищаемой поверхности.

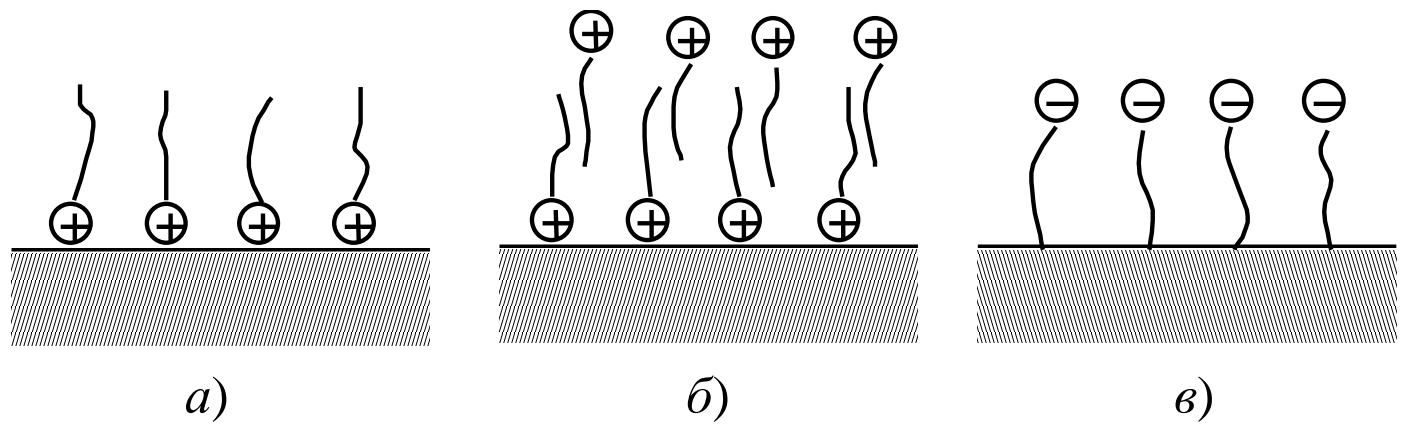
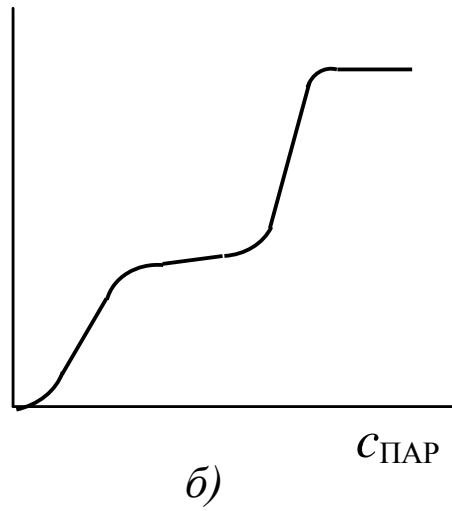
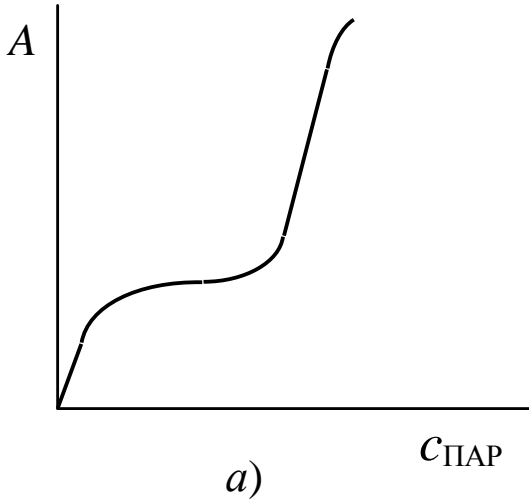
3. Диспергирующее действие ПАВ сводится к приданию агрегативной устойчивости твердым и жидким (масляным) частичкам загрязнений, то есть к суспендированию или эмульгированию.

В свою очередь, лиофилизация отмываемой поверхности препятствует ресорбции загрязнений.

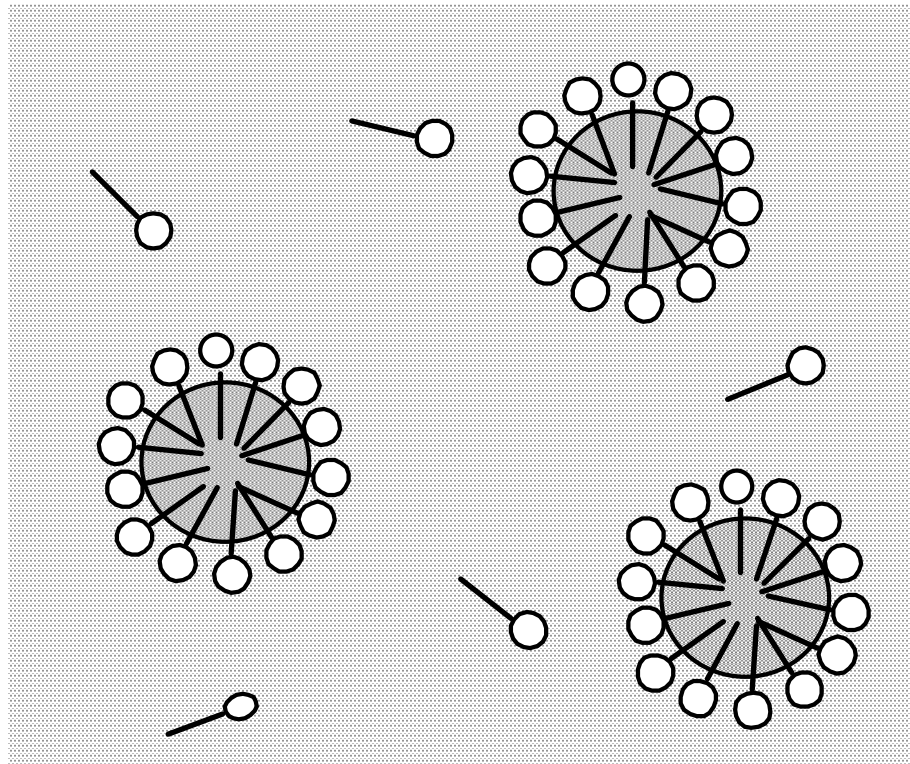
4. Ионные коллоидные ПАВ являются мощными пенообразователями, которые стабилизируют пену. Вспенивание же способствует как механическому удалению, так и флотации загрязнений.

5. Вероятно, загрязнения масляного характера могут солюбилизоваться внутри мицелл ПАВ. Такая точка зрения естественна, поскольку моющее действие наблюдается лишь при концентрациях, превышающих ККМ.

# Изотермы адсорбции ПАВ

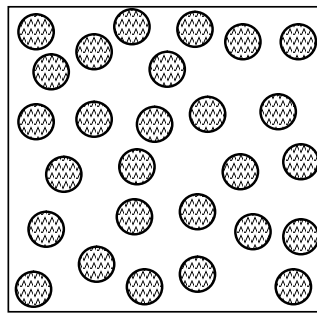
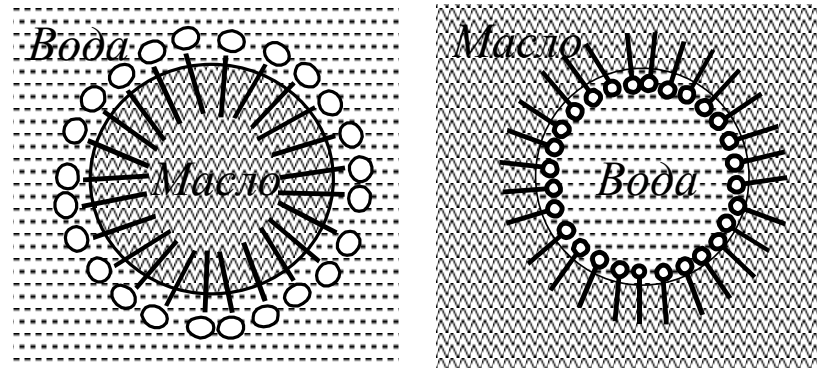


Адсорбция ПАВ на твердых поверхностях  
(на примере отрицательно заряженной поверхности)

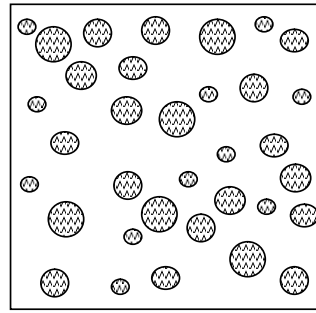


Капли эмульсии типа м/в, стабилизированные ПАВ

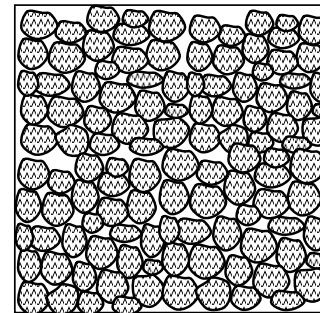
# Эмульсии прямые и обращённые



*a)*



*б)*

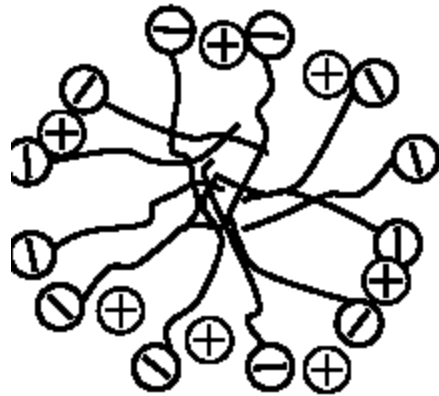


*в)*

*a)* – монодисперсная эмульсия; *б)* – полидисперсная эмульсия;  
*в)* – высококонцентрированная эмульсия

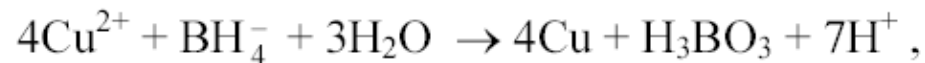
# Использование нанореакторов – мицелл ПАВ

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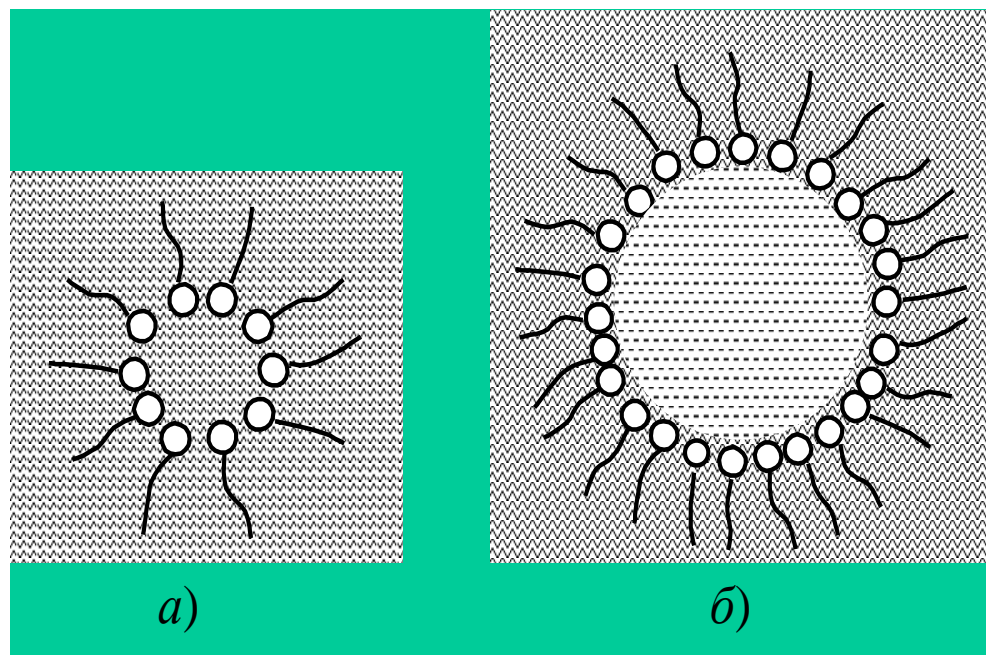
Синтезы коллоидных частиц металлов целесообразно проводить в присутствии стабилизаторов – высокомолекулярных соединений или коллоидных ПАВ.

Методы, в которых катионы металлов вводятся в раствор в виде мицелл ПАВ. Например, на водный мицеллярный раствор *n*-додецилсульфата меди действуют восстановителем:



При этом анионы ПАВ  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-$  адсорбируются на поверхности наноразмерных частиц гидрозоля меди, снижая избыточную поверхностную энергию и стабилизируя систему.

Обычные химические реакции проходят в небольших “лужах” (или “каплях”) воды, диспергированной в органическом растворителе:



Это обуславливает наноразмерность новой твердой фазы, которая возникает во время реакции, например:

