Micelle Formation

Lecture: Colloidal Phenomena

Arne Thomas,
MPI of Colloids and Interfaces, Golm
thomas@mpikg.mpg.de
0331-567 9509
What is a Colloid?

Colloid science is the study of systems involving small particles of one substance suspended in another.

Colloid chemistry is closing the gap between molecular chemistry and solid state properties!
Micelles ("Aggregation colloids")

Outline

1. Surfactants/Introduction
2. Basics of micellization: characterization and properties
3. Micelle formation mechanism
4. Semiquantitative predictive models of micellization
   (Tanford, Israelachvili, Ruckenstein, Nagarajan)
5. What is the “deeper” reason for self-assembly?
1. Surfactants

**Ionic surfactants**

- **Cationic**
  - \( \text{N}^+ \text{Br}^- \)

- **Anionic**
  - \( \text{SO}_4^2^- \)
  - \( \text{SO}_3^- \)
  - Phenol
  - \( \text{CO}_2^- \)

**Non-ionic surfactants ("Niotenside")**

- \( \left[ \text{PEO} \}_{n} \left[ \text{PPO} \}_{m} \right. \) \( \text{OH} \) "Brij"

**Pluronics:** \( \text{PEO} - \text{PPO} - \text{PEO} \)
1. Surfactants

Zwitterionic surfactants: Phospholipids

Phospholipids are the building block of biological membranes

Phosphatidylcholin (Lecithin)
Introduction: Self-assembly of surfactants in water

Formation of liquid crystals („lyotropic mesophases“) upon increase in the surfactant concentration

Surfactant volume fraction $\phi$
Why are micelles/self-assembled structures of interest at all?

1) Living organisms:

Cells = vesicles

2) Applications of surfactants:

Cleaning/Detergents (40%), Textiles, Cosmetics, Paper Production, Paint, Food, Mining (Flotation)......

Surfactant production per year: ~40 billion tons
3) Chemical reactions in micelles:


The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals

Micelles as „nanoreactors“

Emulsion polymerisation

4) New materials through templating/casting

EtOH/H$_2$O

Si(OH)$_4$

Porous material

SiO$_2$
What happens during washing?

Solubilization by micelles

Chiuz, 2003
2. Basics of micellization: characterization and properties

Contents of this chapter:

- Characterization of micelles
- Basic properties of micelles
- The critical micelle concentration
- The Krafft temperature
Different shapes of micelles

What determines the shape/size of micelles...?

- Head group size?
- Ionic strength?
- Hydrophobic tail?
A didactic excursion: wrong illustrations of micelles

Standard figure seen in textbooks:

Wrong:
1. There is no denser core!
2. The heads are not so perfectly arranged
3. For normal surfactants, micelles are not shape-persistent

A more realistic illustration of micelles:

Pluronics: up to 30% of the core is water
Can micelles be seen by microscopic techniques?

Special preparation techniques necessary:
„Cryo Transmission Electron microscopy“ (Cryo-TEM)


Preparation:
1) Controlled environmental chamber to minimize compositional changes

2) rapid thermal quenching of a thin layer of the sample in a liquid ethane slush (formation of vitrified ice).
Visualization of self-assembled structures

Cylindrical micelles forming a stable 2D hexagonal lattice in a SiO$_2$ matrix

Pore structures can be seen as „cast“ of the micellar structure (Nanocasting)
Shape persistent micelles

“The first account of a structurally persistent micelle”
Böttcher et al.
*Angew. Chemie*, 2004, 43, 2959

Specific interactions / covalent linkages can lead to micelles, which do not change their size/shape!
Characterization of micelles

TEM, light scattering, surface tension, spectroscopy, ...

...but, just informations about the size, shape ... of the overall micelle

What evidence does exist that the general core-shell picture of micelles is correct?

A non-invasive technique with nanometer resolution is needed
Small-angle scattering of micellar objects

Coherent scattering of x-rays or neutrons:

\[ I(2\theta) = \text{function}(\rho(r)) \]
Contrast matching technique for small-angle neutron scattering

Poly(styrene)-b-poly(4-pyrrolidone) forms inverse micelles in toluene

$\text{PS}_{120,d8}$-$\text{P4VP}_{118}$

deuterated PS

toluene

hairy micelles
Poly(styrene)-b-poly(4-pyrrolidone) forms inverse micelles in toluene

Poly(styrene)-b-poly(4-pyrrolidone) forms inverse micelles in toluene

Results:

$R_{\text{Core}} = 12 \text{ nm}$, $R_{\text{micelle}} = 36 \text{ nm}$
The critical micelle concentration (cmc, $c_k$)

1. Small $c$: Adsorption of surfactants at the air-water interface
2. $c >$ cmc: formation of micelles

$\text{cmc (}c_k\text{)} = \text{critical micelle concentration:}$

concentration, above which micelles are observed

$$\Delta G_{\text{mic}}^\circ = \mu_{\text{mic}}^\circ - \mu_{\text{solv}}^\circ = RT \ln (\text{cmc})$$
The critical micelle concentration (cmc, $c_k$)

Surface tension at cmc

Abrupt changes at the cmc due to micelle formation!

cmc of nonionic surfactants is generally lower compared to ionic surfactants
The critical micelle concentration (cmc, $c_k$)

Typical behavior of selected physico-chemical parameters such as the equivalence conductivity $\Lambda_c$ or the surface tension $\sigma$ on the surfactant concentration.

Ionic surfactants
Conductivity: $\Lambda_c \approx \mu$ (mobility)

Abrupt changes at the cmc due to micelle formation!
Influence of the surfactant structure on the cmc: tail length

The cmc decreases with increasing tail length because the hydrophobic character increases

Ionic surfactants
Conductivity:
\[ \Lambda_c \approx \mu \text{ (mobility)} \]
Summary: Some values about micelles

Micelle size:
- 3 - 50 nm

Aggregation number:
- Ionic surfactants
  - $z_A = 10^{-170}$
- Nonionic surfactants
  - $z_A = 30 - 10,000$

Critical micelle concentrations (CMC):
- cmc of ionic surfactants
  - is generally higher
  - compared to nonionic surfactants

- Ionic surfactants
  - cmc = $10^{-3} - 10^{-2}$ M

- Nonionic surfactants
  - cmc = $10^{-4} - 10^{-3}$ M
Solubility of surfactants-The Krafft temperature

- Solubility of surfactants highly T dependent
- Solubility is usually low at low T, rising rapidly in narrow range
- No micelles possible above a certain temperature
- The point where solubility curve meets CMC curve is the Krafft point, which defines the $T_{krafft}$.
- The Krafft temperature can be regarded as a „melting point“
3. Micelle formation mechanism

Stepwise growth model (Isodesmic model)

S: surfactant molecule

- \( S + (n-1)S \Leftrightarrow S_2 + (n-2)S \Leftrightarrow S_{n-1} + S \Leftrightarrow S_n \)

- Aggregation is a continuous process (broad aggregation, no cmc)

- Distribution of species

Not in agreement with sudden changes at cmc
3. Micelle formation mechanism

Closed aggregation model

aggregation number $n$ dominates
- (when $n \to \infty$, phase separation model)

$\text{cooperative phenomenon!}$

$K_n = \frac{[\text{micelles}]}{[\text{monomers}]^n} = \frac{[S_n]}{[S]^n}$

$\text{CMC} = (nK_n)^{-1/n}$

$nS \Leftrightarrow Sn$, eq.

$K_n = 10^{30}; n=20$

\[ \text{[monomer]} \]

\[ \text{c-[monomer]} \]
4. Semiquantitative predictive models of micellization

Contents of this chapter:

• Concept of the packing parameter (Israelachvili, 1976) for the prediction of micelle shapes and sizes
• Which energetic contributions determine the micellization? (Tanford-modell + extension by Nagarajan and Ruckenstein)
• Application to basic features of micellization
The concept of the “packing parameter $P$” (Israelachvili, 1976)

$P = \frac{V_0}{a_e l_0}$

- $V_0$: surfactant tail volume
- $a_e$: equilibrium area per molecule at the aggregate interface
- $l_0$: tail length

Common surfactants:
$v_0/l_0 = \text{const.} = 0.21 \, \text{nm}^2$ (single tail)

Example: Spherical micelle with aggregation number $g$

$V_{\text{core}} = g \cdot V_0 = 4\pi R^3/3$

$A = g \cdot a_e = 4\pi R^2$

$R = 3 \cdot \frac{V_0}{a_e}$

With $R \leq l_0 \quad \Rightarrow \quad 0 \leq \frac{V_0}{a_e l_0} \leq 1/3$
The concept of the “packing parameter P” (Israelachvili)

Prediction of the shape of self-assembled structures in solution

**Table 1. Geometrical Relations for Spherical, Cylindrical, and Bilayer Aggregates**

<table>
<thead>
<tr>
<th>variable</th>
<th>sphere</th>
<th>cylinder</th>
<th>bilayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume of core</td>
<td>$4\pi R^3/3$</td>
<td>$\pi R^2$</td>
<td>$2R$</td>
</tr>
<tr>
<td>surface area of core</td>
<td>$4\pi R^2$</td>
<td>$2\pi R$</td>
<td>$2$</td>
</tr>
<tr>
<td>area per molecule $a$</td>
<td>$3v_0/R$</td>
<td>$2v_0/R$</td>
<td>$v_0/R$</td>
</tr>
<tr>
<td>packing parameter $v_0/al_0$</td>
<td>$v_0/al_0 \leq 1/3$</td>
<td>$v_0/al_0 \leq 1/2$</td>
<td>$v_0/al_0 \leq 1$</td>
</tr>
<tr>
<td>largest aggregation number $g_{max}$</td>
<td>$4\pi l_0^3/3v_0$</td>
<td>$\pi l_0^2/v_0$</td>
<td>$2l_0/v_0$</td>
</tr>
<tr>
<td>aggregation number $g$</td>
<td>$g_{max} (3v_0/al_0)^3$</td>
<td>$g_{max} (2v_0/al_0)^2$</td>
<td>$g_{max} (v_0/al_0)$</td>
</tr>
</tbody>
</table>

**Common surfactants:**

$v_0/l_0 = \text{const.} = 0.21 \text{ nm}^2$ (single tail)

- Only the headgroup controls the equilibrium aggregate structure via the headgroup area $a_e$
- The tail does not have any influence on the shape and size of the aggregate
The concept of the “packing parameter $P$” (Israelachvili)

Table 2.1  Expected aggregate characteristics in relation to surfactant critical packing parameter, $P_c = \sqrt[3]{a_o/c}$

<table>
<thead>
<tr>
<th>$P_c$</th>
<th>General Surfactant type</th>
<th>Expected Aggregate Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.33</td>
<td>Single-chain surfactants with large head groups</td>
<td>Spherical or ellipsoidal micelles</td>
</tr>
<tr>
<td>0.33 - 0.5</td>
<td>Single-chain surfactants with small head groups, or ionic species in the presence of large amounts of electrolyte</td>
<td>Large cylindrical or rod-shaped micelles</td>
</tr>
<tr>
<td>0.5 - 1.0</td>
<td>Double-chain surfactants with large head groups and flexible chains</td>
<td>Vesicles and flexible bilayers structures</td>
</tr>
<tr>
<td>1.0</td>
<td>Double-chain surfactants with small head groups or rigid, immobile chains</td>
<td>Planar extended bilayers</td>
</tr>
<tr>
<td>&gt;1.0</td>
<td>Double-chain surfactants with small head groups, very large and bulky hydrophobic groups</td>
<td>Reversed or inverted micelles</td>
</tr>
</tbody>
</table>

Figure 2.6  Changes in the critical packing parameters ($P_c$) of surfactant molecules give rise to different aggregation structures.

- Negative or reversed curvature ($P > 1$)
  - Water-in-oil
  - Oil-soluble micelles

- Zero or planar curvature ($P \approx 1$)
  - Bicontinuous

- Positive or normal curvature ($P < 1$)
  - Water-soluble micelles
  - Oil-in-water microemulsions
Predictions of the “packing parameter concept”

“Big headgroup” = large $a_e$:

“Small headgroup” = small $a_e$:
Predictions of the “packing parameter concept”

**A model surfactant system**

Reports

Self-Assembly of Mesoscopic Metal-Polymer Amphiphiles

Sungho Park, Jung-Hyuk Lim, Sung-Wook Chung, Chad A. Mirkin

starting from commercial anodic alumina

electro-deposition of gold

polymerization of polypyrrole

dissolution of the alumina membrane and the silver cathode and backing
Predictions of the “packing parameter concept”

A model surfactant system

block length ratio (Au/PPy)

3:2 4:1 1:4

explanation of the self-assembly by use of the concept of the packing parameter

\[ R = \frac{V}{a_h l_c} \]

Hydrophobic attraction
The free energy model by Tanford

"Phase separation model": micelles are "microphase"

\[
\left( \frac{\Delta \mu^0_g}{kT} \right) = \left( \frac{\Delta \mu^0_g}{kT} \right)_{\text{Transfer}} + \left( \frac{\Delta \mu^0_g}{kT} \right)_{\text{Interface}} + \left( \frac{\Delta \mu^0_g}{kT} \right)_{\text{Head}}
\]

Avoiding the contact between hydrocarbon bails and water

Chemical potential change

Residual contact water – hydrocarbon:
\[ \sigma \cdot a \]

Head group repulsion:
\[ \alpha / a \]
The free energy model by Tanford and the equilibrium headgroup area $a_e$

Micelles in thermodynamic equilibrium:

$$
\frac{\partial}{\partial a} \left( \frac{\Delta \mu^o_g}{kT} \right) = 0 \Rightarrow \left( \frac{\sigma}{kT} \right) - \left( \frac{\alpha}{kT} \right) \frac{1}{a^2} = 0 \text{ at } a = a_e \Rightarrow
$$

$$
\sigma : \text{ interfacial tension} \quad \alpha : \text{ headgroup repulsion parameter}
$$

$$
a_e = \left( \frac{\alpha}{\sigma} \right)^{1/2} \quad g \propto \frac{1}{a_e}
$$

General aspects:

1) **Tail transfer** is responsible for aggregation, no influence on size and shape!

2) **Residual contact** $\propto a_e$ → promotion of the growth of aggregates

3) **Headgroup repulsion** $\propto \frac{1}{a_e}$, → limitation of the aggregate size!

Tanford’s model explains basic features of micellization!
Some successful predictions of the packing model

\[ a_e = \left( \frac{\alpha}{\sigma} \right)^{1/2} \quad \text{P}= \frac{V_0}{(a_e I_0)} \]

1) Nonionic surfactants with ethylene oxide headgroups

A) \( m \) small \( \rightarrow \) \( \alpha \) small \( \rightarrow \) \( a_e \) small

\[ \frac{V_0}{(a_e I_0)} \text{ large} \rightarrow \text{bilayers/lamellae favored} \]

B) \( m \) larger \( \rightarrow \) \( \frac{V_0}{(a_e I_0)} \) lower \( \rightarrow \) cylindrical micelles favored

2) Ionic surfactants:

salt addition decreases the repulsion \( \alpha \) \( \rightarrow \) decrease in \( a_e \)

increase in \( \frac{V_0}{(a_e I_0)} \)

\( \rightarrow \) transition from spherical micelles to cylindrical micelles.
Some successful predictions of the packing model

\[ a_e = \left( \frac{a}{\sigma} \right)^{1/2} \quad P = \frac{V_0}{(a_e l_0)} \]

3) Single tail / double tail surfactants

\[ \text{Same equilibrium area } a_e \]

\[ \rightarrow V_0/(a_e l_0) \text{ twice as large for double tail} \]

\[ \rightarrow \text{bilayers instead of spherical or globular micelles} \]

4) Influence of solvents

\[ \text{Interfacial tension } \sigma \text{ decreases} \]

\[ \rightarrow a_e \text{ increases} \rightarrow V_0/(a_e l_0) \text{ decreases} \]

\[ \rightarrow \text{bilayer to micelles, rodlike to spherical micelles} \]
The Tanford model predicts various experimental findings and supports the “packing parameter” concept!

\[ a_e = \left( \frac{\alpha}{\sigma} \right)^{1/2} \]

\[ P = V_0 / (a_e l_0) \]

5) Influence of temperature

Increasing the temperature decreases the steric repulsion of PEO headgroup

\[ \alpha \text{ decreases} \rightarrow a_e \text{ decreases} \]

\[ \rightarrow P \text{ increases} \]

\[ \rightarrow \text{transition from spherical micelles to cylindrical micelles.} \]
Attention! Possible misinterpretation of the packing parameter $P$

Straightforward interpretation of the molecular packing concept

Geometric head group area

Small tail

Large tail

$P_{\text{small tail}} = P_{\text{large tail}}$ ?

• Are the assumptions of the “packing parameter” model incorrect?

• How does the tail influence self-assembly?

Same aggregation behavior? … obviously not!
ATTENTION: Neglected role of the surfactant tail!!

- What is the role of the tail?
- Is there a misinterpretation of the Tanford model?

... Let’s have a closer look on the model again...

\[ P = \frac{V_0}{(a_e l_0)} \]

\( a_e \): is an equilibrium parameter, not just a geometrical surface area!

The tail might influence the packing parameter \( \alpha \) and thereby the aggregation.
Influence of tail packing constraints

Different packing for the hydrocarbons compared to the bulk: Non-uniform deformation in the micelle!

\[
\left( \frac{\Delta \mu_g^o}{kT} \right) = \left( \frac{\Delta \mu_g^o}{kT} \right)_{\text{Transfer}} + \left( \frac{\Delta \mu_g^o}{kT} \right)_{\text{Interface}} + \left( \frac{\Delta \mu_g^o}{kT} \right)_{\text{Head}} + \left( \frac{\Delta \mu_g^o}{kT} \right)_{\text{Packing}}
\]

(Nagarajan, Ruckenstein)
The hydrocarbon chains have to deform non-uniformly to fill the core with uniform density.

\[
\left( \frac{\Delta \mu^o_g}{kT} \right)_{\text{Packing}} = \left( \frac{3\pi^2}{80} \right) \frac{R^2}{NL^2} = \frac{Q}{a^2}, \quad \text{(for spheres)}
\]

\[
\frac{\partial}{\partial a} \left( \frac{\Delta \mu^o_g}{kT} \right) = 0 \Rightarrow \left( \frac{\sigma}{kT} \right) - \left( \frac{\alpha}{kT} \right) \frac{1}{a^2} - \frac{2Q}{a^3} = 0
\]

at \( a = a_e \Rightarrow a_e = \left( \frac{\alpha}{\sigma} + \frac{2Q/a_e}{\sigma/kT} \right)^{1/2} \)

L = characteristic segment length  
N = number of segments  
R = radius of micelle

\[ Q \propto L, v_0 \]

The equilibrium head group area (\(a_e\)) is dependent on the length of the hydrophobic tail!!

Shape transitions possible with varying tail length!
Influence of tail packing constraints - simulations

“classical” packing model

\[ a_e = \left( \frac{\alpha}{\sigma} \right)^{1/2} \]

Consideration of tail packing constraints

\[ a_e = \left( \frac{\alpha}{\sigma} + \frac{2Q/a_e}{\sigma/kT} \right)^{1/2} \]

<table>
<thead>
<tr>
<th>nC</th>
<th>( a_e ) (Å²)</th>
<th>( v_0/a_eI_0 )</th>
<th>( a_e ) (Å²)</th>
<th>( v_0/a_eI_0 )</th>
<th>( a_e ) (Å²)</th>
<th>( v_0/a_eI_0 )</th>
<th>( a_e ) (Å²)</th>
<th>( v_0/a_eI_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>50</td>
<td>0.42</td>
<td>(59.6)</td>
<td>(0.352)</td>
<td>57.5</td>
<td>0.365</td>
<td>(54.1)</td>
<td>(0.388)</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>0.42</td>
<td>62.9</td>
<td>0.334</td>
<td>60.1</td>
<td>0.349</td>
<td>(55.7)</td>
<td>(0.377)</td>
</tr>
<tr>
<td>16</td>
<td>50</td>
<td>0.42</td>
<td>65.7</td>
<td>0.320</td>
<td>62.5</td>
<td>0.336</td>
<td>(57.2)</td>
<td>(0.367)</td>
</tr>
</tbody>
</table>

For \( \sigma/kT = 0.12 \text{ Å}^{-2} \), \( \alpha/kT = 300 \text{ Å}^2 \)

Cylindrical micelles

Spherical micelles possible!!

The tail length influences the head group area and thereby the shape!
Why don’t oil and water mix? The “hydrophobic effect”

1) Micellization

2) Hydrocarbons in water

Why unfavorable?
Entropie/enthalpy of micellization

\[ \Delta G = \Delta H - T \Delta S \]

Low-molecular weight surfactants:

- \( \Delta H \) ca. + 1-2 kJ/mol
  Micellization is unfavorable with respect to the enthalpy!!

- \( \Delta S \) ca. + 140 J/K: The entropy of micellization is POSITIVE

Specific features of the solvent (water) enable micellization!

* High surface tension,
* very high cohesion energy,
* high dielectric constant, high boiling point, etc etc
Water is not a normal liquid! The “iceberg model”


A) Nonpolar solutes create a clathrate-like cage of first-shell waters around the solute.

B) Large entropic cost to order the hydrogen bonds into a more open “iceberg”-like structure (low temperature).

C) High-Temperatures break hydrogen bonds to gain entropy, at the cost of the enthalpy.

D) Analogy: Clathrate formation of rare gases in water.
Small-Size Model: Is the disaffinity of oil for water due to water’s small size?

The high cost in free energy comes from the difficulty of finding an appropriate cavity in water, due to the small size of water molecules.

Free-volume distribution of a simple liquid (n-hexane) and water
Literature:

Thermodynamics:

Visualization of micelles:

Washing/surfactants:

Hydrophobic effect:
Thank you!!