Colloid Chemistry

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Surfactants: micellization

- Hydrophobic group
- Hydrophilic group

Dilution to equilibrium

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The surfactant concentration above which molecular aggregates, termed “micelles”, begin to spontaneously form. In practice, a narrow range of surfactant concentrations represents the transition from a solution in which only single, unassociated surfactant molecules (monomers) are present to a solution containing micelle.

Dictionary of colloid and interface science - L.L. Schramm

The threshold at which micellization begins
Critical Micelle Concentration (CMC)

Only surfactant monomers (c<CMC)

Micelles begin to form (c≈CMC)

More micelles [monomers]≈CMC
Micellization of gemini surfactants

(a) Micellar phase
Water phase

(b) Micellar phase
Water phase
Surfactants: micellization

Requirements:

- Charged head group
- Zwitterion head group
- Bulky oxygen-containing head group

With long chain alcohols, amides or amines, micellization does not occur

- Significant hydrogen bonding
- Significant dipolar interaction with water

Exchange rate in μs regime (entry/exit)
Critical Micelle Concentration (CMC)

(A) Surface Tension, mNm\(^{-1}\)
- Critical Micelle Concentration (CMC)
- Monomer
- Micelle

(B) Physical Properties
- Osmotic Compressibility
- Solubilization
- Turbidity
- Self Diffusion

Critical Micelle Concentration (CMC)
Critical Micelle Concentration (CMC)

C < CMC: strong electrolyte solution
C > CMC: properties compatible with presence of colloids

1. Turbidity increase due to the formation of aggregates
2. Conductivity: decrease at CMC owing to the lower mobility of the larger micelles

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Micellization: the «reaction» model

\[ nS \leftrightarrow S_n \]

Clustering: reversible process (\(\rightarrow\) dilution shifts reaction to monomeric surfactant)

\[ n = \text{degree of aggregation} \]

If a ionic surfactant \(S^-M^+\) is involved (assumption: anionic surfactant):

\[ nS^- + mM^+ \leftrightarrow (S_n^-M_{m}^+)^{z^-} + zM^+ \]

\( n = \text{degree of aggregation}, \ z = n-m \)

ensuring electroneutrality

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### Critical Micelle Concentration (CMC)

**TABLE 8.1** Critical Micelle Concentration, Degree of Aggregation, and Effective Fractional Ionization for Several Surfactants With and Without Added Salt

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Solution</th>
<th>Critical micelle concentration (mole liter(^{-1}))</th>
<th>Aggregation number (n)</th>
<th>Ratio of charge to aggregation number, (z/n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>Water</td>
<td>0.00810</td>
<td>80</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>0.02 M NaCl</td>
<td>0.00382</td>
<td>94</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.03 M NaCl</td>
<td>0.00309</td>
<td>100</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.10 M NaCl</td>
<td>0.00139</td>
<td>112</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.20 M NaCl</td>
<td>0.00083</td>
<td>118</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.40 M NaCl</td>
<td>0.00052</td>
<td>126</td>
<td>0.13</td>
</tr>
<tr>
<td>Dodecylamine hydrochloride</td>
<td>Water</td>
<td>0.01310</td>
<td>56</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.0157 M NaCl</td>
<td>0.01040</td>
<td>93</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.0237 M NaCl</td>
<td>0.00925</td>
<td>101</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.0460 M NaCl</td>
<td>0.00723</td>
<td>142</td>
<td>0.09</td>
</tr>
<tr>
<td>Decyl trimethyl ammonium bromide</td>
<td>0.013 M NaCl</td>
<td>0.06800</td>
<td>36</td>
<td>0.25</td>
</tr>
<tr>
<td>Decyl trimethyl</td>
<td>Water</td>
<td>0.06800</td>
<td>36</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.01530</td>
<td></td>
<td>50</td>
<td>0.21</td>
</tr>
<tr>
<td>Dodecyl trimethyl</td>
<td>Water</td>
<td>0.01070</td>
<td>56</td>
<td>0.17</td>
</tr>
<tr>
<td>ammonium bromide</td>
<td>0.013 M NaCl</td>
<td></td>
<td>56</td>
<td>0.17</td>
</tr>
<tr>
<td>Tetradecyl trimethyl</td>
<td>Water</td>
<td>0.00302</td>
<td>75</td>
<td>0.14</td>
</tr>
<tr>
<td>ammonium bromide</td>
<td>0.013 M NaCl</td>
<td>0.00180</td>
<td>96</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Aggregation number $n$ and other facts

1. All other things being equal, the aggregation number $n$ increases as the length of the hydrocarbon chain increases.
2. The aggregation number for sodium dodecyl sulfate increases with increasing amounts of the indifferent electrolyte NaCl.
3. General tendency for CMC to decrease owing to the addition of electrolyte
4. Order of ion binding to negative micelles is $\text{Cs}^+ > \text{Rb}^+ > \text{Na}^+ \text{ Li}^+ +$ and for positive micelles $\text{I}^- > \text{Br}^- > \text{Cl}^-$: larger ions that are more polarizable $\rightarrow$ less hydrated bind more effectively.
5. For nonionics, increasing the polyoxyethylene chain length for a constant R group decreases $n$.
6. Factors that increase $n$ tend to lower the CMC.
7. At the CMC, many micelles are roughly spherical and relatively monodisperse.
Adopted models:

1. Law of mass action approach (better for non aqueous systems, \( n < 10 \))

2. Phase equilibrium approach (better for aqueous systems, \( n \approx 50-100 \))
Micellization: thermodynamics

1. Law of mass action approach (MA) («chemical reaction»)
2. Phase equilibrium approach (PE) («phase equilibrium»)

\[ 2S \leftrightarrow S_2 \leftrightarrow S_3 \leftrightarrow S_4 \leftrightarrow S_n \]

\[ nS^- + mM^+ \leftrightarrow (S_n^-M_m^+)z^- + zM^+ \]

\[ z = n - m; \]

For \( m=0, z=0 \): non-ionics surfactants

Increasing \( S \) concentration shifts equilibrium to the right

Micelles however form only above CMC (\( n \approx 50 \))

Above CMC, \( S \) varies little (PE approach describes it better)

Aggregation also in non-aqueous medium (\( n < 10 \)) (MA approach)
Micellization: thermodynamics

1. Law of mass action approach («chemical reaction»)
2. Phase equilibrium approach («phase equilibrium»)

\[ nS^- + mM^+ \rightleftharpoons (S_n^-M_m^+)^{z-} \quad z = n-m \]

\[ K = \frac{a_{mic}}{a^n_s a^m_M} \]

\[ \Delta G^0 = -RT \ln K = -RT (\ln a_{mic} - n \ln a_s - m \ln a_M) \]
Micellization: thermodynamics

divide by n: free energy change per mole of surfactant $\Delta G_{mic}^0$

At CMC, $a_m \approx a_s = a_{CMC}$

$$\Delta G_{mic}^0 = RT \left[ \left( 1 + \frac{m}{n} \right) \ln a_{CMC} - \frac{1}{n} \ln a_{mic} \right]$$

n at CMC is large, therefore $-\frac{1}{n} \ln a_{mic}$ can be neglected:

$$\Delta G_{mic}^0 \approx RT \left[ \left( 1 + \frac{m}{n} \right) \ln a_{CMC} \right] \approx RT \left[ \left( 1 + \frac{m}{n} \right) \ln c_{CMC} \right]$$
Micellization: thermodynamics

\[ \Delta G_{mic}^0 \approx RT \left[ \left(1 + \frac{m}{n}\right) \ln c_{CMC} \right] \]

\( m = 0 \) for **non ionics**:  
\[ \Delta G_{mic}^0 \] describes the *contribution of the surfactant alone*  
without including the contribution of counterion binding  
It can be determined by CMC

\[ \Delta G_{mic}^0 \approx RT \left[ \ln c_{CMC} \right] \]
Micellization: thermodynamics

1. Law of mass action approach

2. Phase equilibrium approach

define the **standard state** for \( \Delta G^0_{\text{mic}} \)

Depends on the units we use using mole fractions:

\[
\Delta G_{\text{mic}}^0
\]

free energy difference per mole between surfactant in **micelles** and in **water**

\[2S \leftrightarrow S_2 \leftrightarrow S_3 \leftrightarrow S_4 \leftrightarrow S^*_n\]

\[nS \leftrightarrow S_n\]

*NB: In this case we neglect counterions*
Micellization: thermodynamics

Thermodynamic criterion for phase equilibrium:

\[ x_s^w + x_s^{mic} = 1 \]

\[ \mu_s^{mic} = \mu_s^w \]

\[ \mu_s = \mu_s^0 + RT \ln \alpha_s \]

For surfactant in water:

\[ \mu_s^w = \mu_s^{0,w} + RT \ln \alpha_s^w = \mu_s^{0,w} + RT \ln f_s^w + RT \ln x_s^w \]

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Micellization: thermodynamics

For the surfactant in water

\[
\mu_S^w = \mu_S^0,w + RT \ln \alpha_S^w = \mu_S^0,w + RT \ln f_S^w + RT \ln x_S^w
\]

Standard state:

- surfactant behaves ideally
- physically: infinite dilute solution of surfactant in water
- Pure surfactant in water

\[
f_S^w \rightarrow 1 \quad \text{and} \quad x_S^w \rightarrow 1
\]

\[
\mu_S^w = \mu_S^0,w
\]

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Micellization: thermodynamics

For the surfactant in the micelle \textit{per mole of micelle} ('): 

\[
(\mu_s^{\text{mic}})' = (\mu_s^{0,\text{mic}})' + RT \ln a_s^{\text{mic}} = (\mu_s^{0,\text{mic}})' + RT \ln f_s^{\text{mic}} + RT \frac{x_s^{\text{mic}}}{n}
\]

Chemical potential of surfactant in micelle \textit{per mole of micelle}

Mole fraction of micelles
Micellization: thermodynamics

For the surfactant in the micelle per surfactant molecule (dividing per n):

\[
\mu_{S,\text{mic}} = \mu_{S,0,\text{mic}} + \frac{RT}{n} \ln f_{S,\text{mic}} + \frac{RT}{n} \ln \frac{x_{S,\text{mic}}}{n}
\]

since it holds condition of equilibrium

\[
\mu_{S,\text{mic}} = \mu_{S,\text{w}}
\]

\[
\mu_{S,0,\text{w}} + RT \ln f_{S,\text{w}} + RT \ln x_{S,\text{w}} = \mu_{S,0,\text{mic}} + \frac{RT}{n} \ln f_{S,\text{mic}} + \frac{RT}{n} \ln \frac{x_{S,\text{mic}}}{n}
\]
Micellization: thermodynamics

\[ \mu_S^{0,w} + RT \ln f_S^w + RT \ln x_S^w = \mu_S^{0,mic} + \frac{RT}{n} \ln f_S^{mic} + \frac{RT}{n} \ln \frac{x_S^{mic}}{n} \]

Assuming that:
1. \( f = 1 \) for both
2. large \( n \) (assumption: \( n \) has only one value, though \( n \) has a distribution of values)

\[ RT \ln x_S^w \gg \frac{RT}{n} \ln \frac{x_S^{mic}}{n} \]

3. knowing that at CMC \( x_s^w \approx c_{CMC} \)

\[ \mu_S^{0,mic} - \mu_S^{0,w} = RT \ln c_{CMC} = \Delta G_{mic}^0 \]

→ difference per mole between the free energy of surfactant in micelle - free energy of surfactant in water

CMC values expressed as mole fractions provide an experimentally viable determination of the free energy change related to aggregation of surfactant molecules to give micells
Thermodynamics of micellization

\[ \Delta H_{\text{mic}}^0 = \left( \frac{\partial (\Delta G_{\text{mic}}^0 / T)}{\partial (1/T)} \right)_p = -T^2 \left( \frac{\partial (\Delta G_{\text{mic}}^0 / T)}{\partial T} \right)_p \]

\[ \Delta G_{\text{mic}}^0 \approx RT \left( 1 + \frac{m}{n} \right) \ln c_{\text{CMC}} \]

\[ \Delta H_{\text{mic}}^0 = RT^2 \left( 1 + \frac{m}{n} \right) \left( \frac{\delta \ln c_{\text{CMC}}}{\delta T} \right)_p \]
Thermodynamics of micellization

\[ \Delta H_0^{mic} = \left[ \delta(\Delta G_0^{mic} / T) / \delta(1/T) \right] \text{ Gibbs-Helmotz equation} \]

\[ \Delta G_0^{mic} \approx RT \left( 1 + \frac{m}{n} \right) \ln c_{CMC} \]

\[ \Delta H_0^{mic} = RT^2 \left( 1 + \frac{m}{n} \right) \left( \frac{\delta \ln c_{CMC}}{\delta T} \right)_p \]

\[ \Delta H \text{ may be calculated from CMC determination plots at various temperatures (CMC vs } T). \]

But: errors in locating the c.m.c. (which in many cases is not a sharp point) lead to a large error in \[ \Delta H \]. A more accurate and direct method of obtaining \[ \Delta H \] is microcalorimetry.
Thermodynamics of micellization

\[ \Delta G^0_{mic} \approx RT \left( 1 + \frac{m}{n} \right) \ln c_{CMC} \]

\[ \Delta H^0_{mic} = RT^2 \left( 1 + \frac{m}{n} \right) \left( \frac{\delta \ln c_{CMC}}{\delta T} \right)_p \]
Thermodynamics of micellization

- by taking \( m = 0 \) we have focused on aggregation of surfactants only
- \( \Delta G^\circ \) values are negative \( \rightarrow \) spontaneous micellization
- \( \Delta H^\circ \) values are both positive or negative
- \( \Delta S^\circ \) values are positive and make a large contribution to \( \Delta G^\circ (\text{driving force}) \): see later

### TABLE 8.3  Some Thermodynamic Properties for the Micellization Process at or Near 25°C for Various Surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( \Delta G^\circ_{mic} ) (kJ mole(^{-1}))</th>
<th>( \Delta H^\circ_{mic} ) (kJ mole(^{-1}))</th>
<th>( \Delta S^\circ_{mic} ) (J K(^{-1}) mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecyl pyridinium bromide</td>
<td>-21.0</td>
<td>-4.06</td>
<td>+56.9</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate(^a)</td>
<td>-21.9</td>
<td>+2.51</td>
<td>+81.9</td>
</tr>
<tr>
<td>( N )-Dodecyl-( N ),( N )-dimethyl glycine</td>
<td>-25.6</td>
<td>-5.86</td>
<td>+64.9</td>
</tr>
<tr>
<td>Polyoxyethylene(6) decanol</td>
<td>-27.3</td>
<td>+15.1</td>
<td>+142.0</td>
</tr>
<tr>
<td>( N ),( N )-Dimethyl dodecyl amine oxide</td>
<td>-25.4</td>
<td>+7.11</td>
<td>+109.0</td>
</tr>
</tbody>
</table>


\(^a\)Calculated in Example 8.4.