Surface chemistry. Liquid-gas, solid-gas and solid-liquid surfaces.

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Surfaces and Interfaces

- Defining of interfacial region
- Types of interfaces: surface vs interface
- Surface tension
- **Contact angle, wetting, and spreading**
- Adsorption
- Biological interfaces
Contact angle

- When a drop of liquid is placed on a solid surface, three interfaces form
- Forces involved: cohesive (between particles of the same phase) and adhesive (between different phases)
- The triple interface formed between solid, liquid, and gas will move in response to the forces arising from the three interfacial tensions until an equilibrium position is established.
- By convention the contact angle is measured in the liquid phase.

\[
\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta
\]

At equilibrium:
\[
\sum \vec{F} = 0
\]
\[
|\vec{F}_{GS}| = |\vec{F}_{LS}| + |\vec{F}_{GL}| \cos \theta
\]
\[
\gamma_{GS} \times l = \gamma_{LS} \times l + \gamma_{GL} \times l \times \cos \theta
\]

we can simplify by \(l\):

\[
\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta
\]

\(\gamma_{GS}\) : surface tension between gas and solid (N/m)
\(\gamma_{LS}\) : surface tension between liquid and solid (N/m)
\(\gamma_{GL}\) : surface tension between gas and liquid (N/m)
\(l\) : length of the triple interface (m)
\(\theta\) : contact angle (°)
**Contact angle and wetting**

When the forces of adhesion are greater than the forces of cohesion, the liquid tends to wet the surface, when the forces of adhesion are smaller than those of cohesion, the liquid tends to "refuse" the surface.
Hydrophobic, hydrophilic surfaces

Low wettability, $\theta>90^\circ$, (Teflon)

High wettability, $\theta<90^\circ$ ($\theta=0^\circ$)

Why does one fabric absorb water well while another seems to refuse it?

www.metacafe.com/watch/21435/magic_sand/
Spreading

When the interfacial tension between the solid and gas phase is larger than the sum of $\gamma_{LS}$ and $\gamma_{GL}$, there is spreading:

$$\gamma_{GS} > \gamma_{LS} + \gamma_{GL} \cos \theta$$

In this case there is no equilibrium position, the contact point keeps advancing along the surface.

The same is true when there is complete wetting, as in this case $\theta=0$ and the triple interface keeps advancing. By combining these, we get for spreading:

$$\gamma_{GS} \geq \gamma_{LS} + \gamma_{GL} \cos \theta$$

when the equality applies for $\theta=0$
Example: ink spreading

Non-spreading liquid gives droplets

\[ \gamma_{SG} < \gamma_{SL} \quad \text{as } \theta=90^\circ \rightarrow \cos \theta = 0 \]

Spreading occurs when a liquid of low surface tension is placed on a surface of high surface tension.

If we know the surface tensions of test inks we can determine the surface tension of a smooth solid surface.

Contact angle between two liquids

A drop of an insoluble oil is placed on a clean water surface it may behave in one of three ways:
1) remain as a **lens**
2) spread as a **thin films**, which may show interference colors until forms as a duplex film (thick enough)
3) spread as a **monolayer**, leaving excess oil as lenses in equilibrium.

In equilibrium:

\[ \gamma_2 = \gamma_{12} \cos \theta_2 + \gamma_1 \cos \theta_1 \]

In the case of spreading:

\[ \gamma_2 > \gamma_{12} \cos \theta_2 + \gamma_1 \cos \theta_1 \]

This is going to stop at the equilibrium if \( \theta_1 \) and \( \theta_2 \neq 0 \) but continues to spread if \( \theta_1 = \theta_2 = 0 \):

\[
\begin{align*}
\gamma_2 & > \gamma_{12} + \gamma_1 \\
\gamma_2 & - (\gamma_{12} + \gamma_1) > 0
\end{align*}
\]

This is defined as the spreading coefficient:

\[ S = \gamma_{\text{lower}} - (\gamma_{\text{upper}} + \gamma_{\text{interface}}) \]

If \( S > 0 \) the liquid will spread, if \( S < 0 \) it will not spread.
Adhesion, Cohesion, Spreading

- The work of adhesion between two immiscible liquids is equal to the work required to separate a unit area of the interface and form two new separate liquid-air interfaces of two pure materials.

- The work of cohesion for a single liquid corresponds to the work required to pull apart a column of liquid of unit cross-sectional area.

\[ W_a = \gamma_B + \gamma_A - \gamma_{AB} \]
\[ W_c = 2\gamma_A \]

Spreading coefficient:

\[ S = W_a - W_c = \gamma_B - (\gamma_A + \gamma_{AB}) \]

\[ S = \gamma_{lower} - (\gamma_{upper} + \gamma_{interface}) \]
Spreading process

Table 4.3  INITIAL SPREADING COEFFICIENTS (IN mN m⁻¹) FOR LIQUIDS ON WATER AT 20°C

(By courtesy of Academic Press Inc.)

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_{W/A}-(\gamma_{O/A}+\gamma_{O/W}) = S$</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexadecane</td>
<td>72.8-(30.0+52.1) = -9.3</td>
<td>will not spread on water</td>
</tr>
<tr>
<td>n-Octane</td>
<td>72.8-(21.8+50.8) = +0.2</td>
<td>will just spread on pure water</td>
</tr>
<tr>
<td>n-Octanol</td>
<td>72.8-(27.5+ 8.5) = +36.8</td>
<td>will spread against contamination</td>
</tr>
</tbody>
</table>

$S=\gamma_{lower}-(\gamma_{upper}+\gamma_{interface})$

$S_i=72.8-(24.8+6.8)=41.2 \text{ mJ/m}^2$

$S_f=28.5-(24.8+6.8)=-2.9 \text{ mJ/m}^2$

Figure 4.16. Spreading of n-hexanol on a water surface
Adsorption and orientation at interface

Figure 4.8. Adsorption of surface-active molecules as an orientated monolayer at air-water and oil-water interfaces. The circular part of the molecules represents the hydrophilic polar head group and the rectangular part represents the non-polar hydrocarbon tail.

Hardy-Harkins rule of the best continuity forms or smooth monotonic transition.
Adsorption and orientation at interface

Hardy-Harkins principle: The best continuity of polarities (smooth transition)

Surface active materials consist of molecules containing both polar and non-polar parts: these molecules are amphiphilic. Materials such as short-chain fatty acids and alcohols are soluble in both water and oil (e.g. paraffin hydrocarbon) solvents. The hydrocarbon part of molecule is responsible for its solubility in oil, whilst the polar –COOH or –OH group has sufficient affinity to water to drag a short-length non-polar hydrocarbon chain into the aqueous solution with it.

Figure 8-5. The orientation of amphipathic molecules at water-air and water-benzene interfaces depends on coverage. Note that benzene competes successfully with the tails for the water surface and also for the other tails, whereas air does not.
Surface tension of mixtures

The surface tensions are not perfectly additive, that means the mole fractions of the components are different at the surface and in the bulk.

The material with lower surface tension tends to accumulate at the surface.
Surface activity

The longer chain compound has the higher surface activity:

\[ \frac{c_{n+1}}{c_n} \approx 3 \]

Many organic solutes, especially polar molecules considerably reduce the surface tension of water. Such solutes tend to accumulate strongly at the surface where in many cases they form a unimolecular film of adsorbed molecules.

*Figure 4.9. Surface tension of aqueous solutions of alcohols at 20°C*
Surface inactivity

Electrolytes (salts, sugar) show surface inactivity.

\[ \gamma = \gamma_0 (1 + kc) \]

canonical

concentration of the surface inactive compound

**Figure 4.10.** Surface tension of aqueous sodium chloride solutions at 20°C
The Gibbs equation

The Gibbs adsorption equation for a dilute solution can be written in two equivalent forms:

\[ \Gamma_i = -\frac{c_i}{RT} \frac{d\gamma}{dc_i} \]

\[ \Gamma_i = -\frac{1}{RT} \frac{d\gamma}{d\ln c_i} \]

\[ \Gamma_i \]: surface excess concentration of component \( i \) (mol/m²)

\[ c_i \]: concentration of component \( i \) in the bulk phase (mol/m³)

\[ \gamma_i \]: surface tension of component \( i \) (N/m)

\[ R \]: gas constant (J mol⁻¹ K⁻¹)

\[ T \]: temperature (K)

It follows from the first equation that \( \Gamma_i \) is positive if \( d\gamma / dc_i \) is negative, that is the surface tension decreases with increasing solute concentration. Surface active materials accumulate but surface inactive materials deplete at the interface.
On the basis of experimental data for surface tension vs. solute concentration the function $d\gamma/dc$ can be determined and the $\Gamma = f(c)$ adsorption isotherm can be calculated.
Gibbs adsorption equation

\[ \Gamma = \Gamma_{\infty} \frac{Bc}{1 + Bc} \]

This is a Langmuir type isotherm (see later)

\[ \frac{c}{\Gamma} = \frac{c}{\Gamma_{\infty}} + \frac{1}{B \Gamma_{\infty}} = \frac{1}{\Gamma_{\infty}} c + \frac{1}{B \Gamma_{\infty}} \]

\[ \Gamma \square \text{ surface excess (mol/m}^2\text{)} \]

\[ \Gamma_{\infty} \square \text{ surface excess at } c=\infty \text{ or maximal } \Gamma \text{ (mol/m}^2\text{)} \]

\[ B \square \text{ isotherm constant (m}^3/\text{mol)} \]

\[ \sigma \square \text{ area occupied by one molecule (m}^2\text{)} \]

\[ \sigma = \frac{1}{\Gamma_{\infty} N_A} \]
Adsorption and orientation at interface

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Hardy-Harkins principle: The best continuity of polarities (smooth transition)

Surface active materials consist of molecules containing both polar and non-polar parts: amphiphilic. Materials such as short-chain fatty acids and alcohols are soluble in both water and oil (e.g. paraffin hydrocarbon) solvents. The hydrocarbon part of molecule is responsible for its solubility in oil, whilst the polar –COOH or –OH group has sufficient affinity to water to drag a short-length non-polar hydrocarbon chain into the aqueous solution with it.
Two-dimensional monolayers can exist in different physical states which bear some resemblance to the solid, liquid and gaseous states in three-dimensional matter.

- Gaseous or vapor films in which the molecules are separate and move about independently. Large compressibility.
- Liquid films, small compressibility.
- Condensed or solid films in which molecules are closely packed and orientated toward the surface.
Monolayer and polymolecular Langmuir - Blodgett (LB) layers

Surface pressure

The surface pressure of the film is determined by measuring the force which must be applied to maintain the float at a fixed position on the surface (located optically) and dividing by the length of the float.

Figure 4.17. The principle of the Langmuir-Adam surface balance

Gaseous films

\[ \pi \sigma = N_A k_B T \]

Liquid-expanded films obey the following equation of state (van der Waals equation)

\[ (\pi - \pi_0)(\sigma - \sigma_0) = N_A k_B T \]
Two-dimensional pressure-area diagrams

- **G**: gas-like phase
- **L₁**: expanded liquid phase
- **L₂**: condensed liquid phase
- **S**: solid phase
Physical state of the monolayers

Schematic diagrams of the main monolayer phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Name</th>
<th>Structure</th>
<th>Smectic category</th>
<th>In-plane area per chain/nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lₑ, L₁</td>
<td>liquid-expanded</td>
<td>random, vertical or tilted</td>
<td>A or C</td>
<td>&gt;0.4</td>
</tr>
<tr>
<td>Lₑ, L₂</td>
<td>liquid-condensed</td>
<td>rectangular (rotator), NN</td>
<td>I</td>
<td>0.198</td>
</tr>
<tr>
<td>Lₑ', L₂'</td>
<td>liquid-condensed</td>
<td>rectangular (rotator), NNN</td>
<td>F or H</td>
<td>0.198</td>
</tr>
<tr>
<td>LS</td>
<td>super-liquid</td>
<td>hexagonal (rotator), V</td>
<td>BH</td>
<td>0.198</td>
</tr>
<tr>
<td>S</td>
<td>solid</td>
<td>rectangular (herringbone), V</td>
<td>E</td>
<td>0.192</td>
</tr>
<tr>
<td>CS</td>
<td>closed-packed solid</td>
<td>rectangular (herringbone), V</td>
<td>Xtal</td>
<td>0.186</td>
</tr>
</tbody>
</table>

NN: chains tilt towards nearest neighbour; NNN: chains tilt towards next nearest neighbour; V: chains are normal to the film surface.
Monolayers

Summary

- Insoluble monolayers are formed from amphiphiles that are virtually insoluble in water. They can be spread on a water surface from drops of a solution of the amphiphile in a volatile solvent or by spontaneous spreading from crystals or drops of the bulk material. Surface balance is used to manipulate monolayers and is a component of various techniques for measuring monolayers properties.

- Monolayers exist in a number of phases, most of which can be compared to smectic phases. The major phases are the S, L (L_{e} and L_{c}) and G. The hydrophilic part of each molecule anchors the molecule to the water surface and the hydrophobic part is in the air and may be disordered, or organized into hexagonal or rectangular patterns.

Molecular size, shape, conformation and packing can be determined
LB transfer on a surface

Substrate Direction

Meniscus Direction

Water subphase

b. No LB transfer on a hydrophilic substrate during downstroke

Substrate Direction

Meniscus Direction

Water subphase

a. Downstroke LB transfer on a hydrophobic substrate
Types of Langmuir—Blodgett films

X (S–A–P–A–P)

Z (S–P–A–P–A)

Y (Substrate–Polar–Apolar–Apolar–Polar)
Langmuir—Blodgett film layers

Y-Type LB film deposition on a hydrophilic substrate (up and down)

Hydrophilic surface

a. First upstroke LB transfer on a hydrophilic substrate
b. Second downstroke LB transfer on a hydrophilic substrate

c. After the third upstroke LB transfer on a hydrophilic substrate
LB layers

First layer tail-to-tail weak, head-to-head strong. Further layer types Y HH, TT, X HT, Z TH. Single layer horizontal technique. Self-assembly.

Figure 5.16  X-type Langmuir–Blodgett film deposition onto a hydrophobic substrate: a. First downstroke. b. Second downstroke. c. After the third downstroke.