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

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http://dragon.unideb.hu/~kolloid/

4. lecture
Contact angle, wetting, and spreading

at equilibrium

\[ \gamma_{SG} = \gamma_{SL} + \gamma_{GL} \cos \theta \]

The triple interface formed between solid, liquid, and gas will move in response to the forces arising from three interfacial tensions until an equilibrium position is established. By convention the contact angle is measured in the liquid phase.

Water contact angles on various solid surfaces.
Paraffin wax : \(110^\circ\). Teflon: \(108^\circ\), polyethylene \(95^\circ\),
mica: \(7^\circ\), gold, glass: \(0^\circ\), Hg on glass \(135^\circ\)

Wettability depends on adhesion /cohesion

4. lecture
Spreading

\[ \gamma_{SG} \geq \gamma_{SL} + \gamma_{GL} \]

\( \gamma_{SG} < \gamma_{SL} \)  Non-spreading liquid gives droplets

Spreading occurs when a liquid of low surface tension is placed on one of high surface tension. If we know the surface tensions of test inks we can determine the surface tension of a smooth solid surface.

\( \gamma_{SG} > \gamma_{SL} \)


4. lecture
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/
Contact angle, wetting, and spreading

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 less by comparison to those of cohesion, the liquid tends to "refuse" the surface.

4. lecture
Contact angle, wetting, and spreading

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.

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

Wettability depends on adhesion /cohesion
The work of **adhesion** between two immiscible liquids is equal to the work required to separate 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 area cross-sectional area.

If $S>0$ will spread, if $S<0$ will not spread
Spreading process $S=\gamma_{\text{low}}-(\gamma_{\text{upper}}+\gamma_{\text{interfac}})$

**Table 4.3** **INITIAL SPREADING COEFFICIENTS (IN mN m$^{-1}$) FOR LIQUIDS ON WATER AT 20°C$^5$**

*(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>

*Figure 4.16. Spreading of $n$-hexanol on a water surface*

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

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

4. lecture
Adsorption and orientation at interface

Hardy-Harkins\'s rule

*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\'s rule of the best continuity forms or smooth monotonic transition

4. lecture
Adsortion and orientation at interface

Hardy-Harkins: 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.

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.
It is not perfectly additive, that means the mole fractions are different at the surface and in the bulk. The material with lower surface tension tends to accumulate at the surface.
Surface activity

Many organic solutes specially 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.

\[ \frac{B_{n+1}}{B_n} \sim 3 \]

The longer chain is the higher surface activity:

\[ Figure 4.9. \ Surface \ tension \ of \ aqueous \ solutions \ of \ alcohols \ at \ 20°C \]

4. lecture
Surface inactivity

Electrolytes show surface inactivity.

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

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

The Gibbs equation can write for a dilute solution in two forms:

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

where \( c_i \) is the concentration (in mol m\(^{-3}\)) of component \( i \) in the solution, \( T \) (K) the absolute temperature, \( R \) the gas constant (8.314 JK\(^{-1}\) mol\(^{-1}\)), \( \gamma \) (Nm\(^{-1}\)) the surface tension and \( \Gamma \) (mol m\(^2\)) is the surface excess concentration. It follows from Equation 1 that \( \Gamma \) is positive if \( d\gamma/dc \) is negative, that is the surface tension decreases with increasing solute concentration. Surface active materials accumulate but surface inactive materials deplete at interface.
Gibbs isotherm

On the basis of experimental surface tension vs. solute concentration function the $d\gamma/dc$ can be determined and the $\Gamma = f(c)$ adsorption isotherm can be calculated.

\[
\Gamma_c = \frac{A}{RT} \frac{Bc}{1 + Bc}
\]

\[
\Gamma_c = -\frac{c}{RT} \frac{d\gamma}{dc}
\]

\[
\Gamma_c = -\frac{1}{RT} \frac{d\gamma}{d\ln c}
\]

slope(tg $\alpha$)
Gibbs adsorption isotherm

\[ \Gamma_c = \frac{A}{RT} \frac{Bc}{1 + Bc} \]

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

\[ \frac{1}{\Gamma}, \text{m}^2 / \text{mol} \quad \frac{1}{\Gamma_\infty N_A} = A_{\text{molekula}} \quad A_m (\text{vagy } \sigma_m, \phi_m) 1 \text{ area occupied by one molecule} \]
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.

Evaporation through monolayers
Monolayer and polymolecular Langmuir-Blodgett (LB) layers

\[ \pi = \gamma_0 - \gamma \]

\[ \pi A = kT \]

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

\[ (\pi - \pi_0)(A - A_0) = kT \]

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.

So far

4. lecture
There are four main phases that can be identified from Pi~A isotherms.

First order transitions between phases should appear as constant pressure regions in the surface pressure-area isotherm.

4. lecture
Physical state of the monolayers

The 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/nm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lc, L$_1$</td>
<td>liquid-expanded</td>
<td>random, vertical or tilted</td>
<td>A or C</td>
<td>&gt;0.4</td>
</tr>
<tr>
<td>Lc, L$_2$</td>
<td>liquid-condensed</td>
<td>rectangular (rotator), NN</td>
<td>I</td>
<td>0.198</td>
</tr>
<tr>
<td>Lc', L$_2'$</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 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

b. No LB transfer on a hydrophilic substrate during downstroke

a. Downstroke LB transfer on a hydrophobic substrate