Adsorption at the liquid/gas interface
1. Surface tension of solutions

In the case of solutions, contrary to pure liquids, simultaneously with the changes of surface area, the surface tension $\gamma$ may change.

If a two-component solution behaves as a regular one, its surface tension changes as a function of the surface composition, according to the equation derived by Prigogine and Defay.

$$\gamma = \gamma_1 x_1 + \gamma_2 x_2 - \beta_p x_1 x_2$$  \hspace{1cm} (1)

where: $\gamma_1$ and $\gamma_2$ are the surface tensions of pure liquid 1 and 2, respectively, $x_1$ and $x_2$ are the molar rations of these liquids, $\beta_p$ is the semi-empirical constant.

Just to recall, a regular solution is a solution that diverges from the behavior of an ideal one only moderately.

For regular solutions:

$$\mu_i - \mu_i^\circ = RT \ln a_i \hspace{1cm} S_i - S_i^\circ = -RT \ln x_i \hspace{1cm} H_i - H_i^\circ = f(x_i) \hspace{1cm} C_{pi} - C_{pi}^\circ = 0$$

Note that the Margules function always contains the opposite mole fraction.

In contrast to the case of ideal solutions, regular solutions do possess an enthalpy of mixing and their volume solutions are not strictly additive and must be calculated from the partial molar volumes that are a function of $x$. 

Adsorption at the liquid/gas interface
The activity coefficients of the liquids (expressed via molar ratio) which form the mixed solutions satisfy the following relations (Margules functions):

\begin{align*}
RT \ln f_1 &= - \alpha x_2^2 \quad (2) \\
RT \ln f_2 &= - \alpha x_1^2 \quad (3)
\end{align*}

A typical mixed solution of two liquids is **acetone-chloroform**, whose surface tension is shown in Fig.1.1.

The surface tensions of these liquids are comparable, \(\gamma = 23.7 \text{ mN m}^{-1}\) for acetone, and \(\gamma = 27.1 \text{ mN m}^{-1}\) for chloroform.

In this system the surface tension changes almost linearly as a function of the solution composition.

**Fig. 1.1.** Changes of the surface tension of acetone/chloroform solution depending on the percent content of chloroform at 18°C. (after E.T. Dutkiewicz, *Fizykochemia Powierzchni*, WNT Warszawa 1998 p. 73).
Fig. 1.2. The isotherm of surface tension of water/methanol solutions depending on the molar ratio of methanol at 293 K (20°C).

However, if the surface tension of one of the two liquids is much lower than the other then even a small amount of the former liquid will reduce the surface tension of the mixed solution. See Fig. 1.2 for the water/methanol solution.
Surface tension of **diluted solutions of organic substances** is described by a semi-empirical **equation of Szyszkowski**.

This equation describes the relationship between the surface tension $\gamma_0$ of the solvent, the surface tension of the solution $\gamma$, and its concentration $c$.

\[
\frac{\gamma_0 - \gamma}{\gamma_0} = B \ln \left(1 + \frac{c}{A}\right)
\]

or

\[
\gamma_0 - \gamma = b \ln (1 + ac)
\]

where $\gamma$ is the surface tension of the solution, $\gamma_0$ is the surface tension of the solvent, $c$ is the concentration of the solution, $B$ and $b$ are the constant characteristic for given homologous series, $a = 1/A$ is called the **specific capillary activity**.

This equation works only in a limited range, for example for fatty acid in the range of 3 – 6 carbon atoms in the chain ($C_3 - C_6$).
2. Surface active substances

Chemical compounds (mostly organic) that reduce surface tension of the solvent already at their very low concentrations are called ‘the surface active agents’ or 'capillary active agents' the commonly used acronym is 'SURFACTANTS', which comes from

SURFace ACTive Agents

The other names sometimes used are detergents and tensydes.

Surfactants are very commonly found in everyday life. The surfactants used for cleaning and washing processes are called 'detergents'. Surfactants are also present in many food products, cosmetics, and hygienic products. They are also produced in living organisms where they play very important physiological functions. Surfactants are also often used in industrial chemical processes, like, plastics, artificial fiber and artificial leather production, crude oil exploitation, and others. Therefore there is continuous need to develop production of new and more efficient surfactants.

Versatile application of surfactants is due to their structure and properties.
A group of surfactants involves many chemical substances having relatively large molecules and amphiphilic, or in other words, amphipatic character.

It means that each molecule contains both a hydrophilic and a hydrophobic (lipophilic) group.

That is, a molecule has a polar, water-soluble group attached to a nonpolar, water-insoluble hydrocarbon chain.

For example, a compound containing a large organic cation or anion which possesses a long unbranched or branched hydrocarbon chain, e.g.

\[
\text{CH}_3(\text{CH}_2)_n\text{COO}^-\text{M}^+
\]

\[
\text{CH}_3(\text{CH}_2)_n\text{N}^+\text{(CH}_3\text{)}_3\text{X}^- \quad (n > 7)
\]

\[
\text{CH}_3(\text{CH}_2)_n\text{SO}_3^-\text{M}^+
\]

The structure of such a molecule is depicted in Fig. 2.1.

**Fig. 2.1.** Chemical structure of a surfactant molecule, A – apolar hydrophobic group, an aliphatic chain, R – the polar hydrophilic functional group.
**The apolar (hydrophobic) part of the molecule** usually consists of 8–18 carbon atoms. In the case of carboxylic acids or natural fats, their derivatives often the chains are not branched, but if the apolar part originates from crude oil or a synthesis process they are mostly branched.

There are also the surfactants whose apolar part consists of an alkylated aromatic ring, the most popular are alkylbenzenes, alkyltoluenes and alkylophenoles with built in one alkyl group of 8–12 carbon atoms, or two alkyl groups of 3–5 C long. Pyridine is often present in the hydrophobic part. Structure of this group, its size and branching have essential significance for the resulting properties of the surfactant.

**The polar part (hydrophilic),** which is responsible for the molecule solubility in water and polar organic solvents, is in most cases acidic or basic. If such a group is present it forms salt with a cation or anion, respectively and becomes soluble.

The most popular polar groups are listed in Table 1.
### Table 1. Typical polar groups found in surfactant molecules.

<table>
<thead>
<tr>
<th>Type</th>
<th>Polar Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic</td>
<td>-COOH</td>
</tr>
<tr>
<td>Sulphate</td>
<td>-OSO$_3$H</td>
</tr>
<tr>
<td>Sulphonate</td>
<td>-SO$_3$H</td>
</tr>
<tr>
<td>Primary amine</td>
<td>-NH$_2$</td>
</tr>
<tr>
<td>Secondary amine</td>
<td>=NH</td>
</tr>
<tr>
<td>Tertiary amine</td>
<td>≡N</td>
</tr>
<tr>
<td>Quaternary ammonium salt</td>
<td>N$^+$</td>
</tr>
<tr>
<td>Pyridine group</td>
<td>C$_6$H$_5$N$^+$</td>
</tr>
</tbody>
</table>
Depending on the chemical character of molecule, surfactants are classified as follows:

**Surfactants**

- **Ionic compounds**
  - **Anionic** (active part of the molecule is an anion)
  - **Cationic** (active part of the molecule is cation)

- **Nonionic surfactants**
  - (their molecules do not form salts)

- **Amphoteric** (both acidic and basic hydrophilic groups are present in the molecule)
3. Traube's rule

Extensive investigations of the surface active substances were conducted by Traube in 1881. He found that in dilute solutions of a homological series, e.g. $R(CH_2)_nX$, each next methylene $-CH_2-$ group in the molecule chain increases the molecule surface activity about 3.2 times ($3.2 \times$).

In other words, to decrease surface tension of a solution by $\Delta \gamma$ it is enough to use 3.2 times lower concentration of next surfactants in the series than the previous one.

Now this is called the Traube's rule. Thus the Traube’s rule relates the surface tension of capillary active organic compounds to the number of the present hydrocarbon $-CH_2-$ groups.
Let us consider two solutions of two surfactants of a homological series whose surface tensions $\gamma$ are the same. Then from the Szyszkowski's equation:

$$\frac{\gamma_o - \gamma}{\gamma_o} = B \ln \left( 1 + \frac{c}{A} \right)$$

it follows that:

$$b_n \ln \left( 1 + \frac{c_n}{A_n} \right) = b_{n+1} \ln \left( 1 + \frac{c_{n+1}}{A_{n+1}} \right)$$

(6)

where $n$ stands for the number of C atoms in the homologue.

Because: $b_n = b_{n+1}$, hence in accordance with the Traube's rule one obtains:

$$\frac{A_n}{A_{n+1}} = \frac{a_{n+1}}{a_n} = \frac{c_n}{c_{n+1}} = 3.2$$

(7)
**Fig. 3.1.** illustrates the changes in the surface tension of the homologous series of carboxylic acid solutions.

*Isidor Traube* (1860–1943) the German physical chemist who founded capillary chemistry and whose research on liquids developed knowledge.

It should be stressed that activity of the surfactants depends also on the solvent properties.
4. Micelles

In the case of so called colloidal electrolytes, like for example myristic acid sodium salt (sodium myristate, sodium tetradecanoate, tetradecanoic acid sodium salt) \( \text{C}_{13}\text{H}_{27}\text{COONa} \), already at its very low concentration 0.01 – 0.02 mol/dm\(^3\) the surface tension decreases sharply and further increase of the compound concentration does not affect the surface tension value. This is a result of formation of so called micelles in the bulk solution, and their concentration is practically constant on the solution surface.

![Fig. 4.1. Changes of surface tension of sodium myristate aqueous solutions.](image)
While in diluted solutions of such kind of surfactants their molecules are present as individual ions or molecules, with the increasing concentration the molecules start to associate between themselves (self-association, self-aggregation) thus forming bigger aggregates called micelles.

**The aggregation takes place when the concentration reaches that characteristic of a given surfactant.**

This concentration is called **Critical Micellization Concentration (CMC).**

At the concentrations larger than CMC, the micelles are formed in the solution.

The micelles can assume different forms, i.e.

- spherical,
- cylindrical,
- disc shape,
- flat, bilayers or multilayers.
Their consistency is **liquid-like**. In Fig. 4.2 there are shown schematically the above mentioned shapes of micelles.

**Fig. 4.2.** Different shapes of micelles in the surfactant solution.
As can be seen in Fig. 4.3, in a non-aqueous solution (organic solvent) reverse micelles are formed, i.e. the hydrophobic tails are directed outward the solution. Inside the micelle there are water molecules that stabilize the micelle. Formation of the micelle is accompanied by abrupt changes in physicochemical properties of the solution.

Fig. 4.3. A) Cross section view of the structures that can be formed by phospholipids in aqueous solutions. B) Scheme of a **micelle** formed by phospholipids in an aqueous solution. C) Scheme of an **inverse micelle** formed by phospholipids in an organic solvent.

[http://en.wikipedia.org/wiki/Micelle]
5. Methods for determination of critical micellization concentration (CMC)

To determine CMC, physicochemical properties of the surfactants are utilized versus the solution concentration. The micelle appearance in solution is accompanied by larger or smaller abrupt changes of the properties. This is plotted in Fig. 5.1.

**Fig. 5.1.** Changes of physicochemical properties of sodium dodecylsulphate (SDS) solution as a function of concentration.

CMC is very often determined from the changes of surface tension versus the solution concentration, as shown in Fig. 5.2.

CMC can be found by extrapolation of the two linear parts of the curve to their crossing point (see Fig. 5.2). Some methods for CMC determination are listed below.

**Measurements:**
- surface tension
- electric conductivity
- refraction index
- light dispersion
- electromotive force
- light absorbance
- polarographic method
- solubilization method

**Fig. 5.2.** Changes of surface tension of a surfactant as a function of log c.
6. Surface tension of inorganic electrolytes

Aqueous solutions of inorganic electrolytes possess larger surface tension than water. The dissolved salt dissociates and the ions appear in the solution. They are located in the bulk solution because of larger dielectric permittivity where the electric field around them can be compensated by the ions hydration. In this way, the system obtains the minimum of free energy. However, the number of free water molecules is reduced.

For example, 5 mol/kg of NaCl solution at 20 °C has the surface tension $\gamma = 81$ mN m$^{-1}$, whereas that of pure water is 72.8 mN m$^{-1}$.
7. Adsorption from the solution at surfactant solution/air interface

For the first time the adsorption process at the solution/gas interface was described by Gibbs in 1878.

Josiah Willard Gibbs
Born: February 11, 1839, New Haven, Connecticut
Died: April 28, 1903 (aged 64) New Haven, Connecticut
Nationality - American
Fields: Physics and Chemistry
Institutions: Yale University
Alma mater: Yale University
Let us consider the following two phase systems.  

**a) Adsorption at the interface between the phases α and β (system I)**

![Diagram of adsorption at the interface between phases α and β](image)

There is a system consisting of the phases α and β separated by the surface XY.

Into the system there is introduced $n_i$ moles of a component „i”.

As a result, it will distribute between the phases α and β. When the equilibrium in the system has established, the concentration of the component $i$ in the phase α amounts $c_{i\alpha}$, and in the phase β it amounts $c_{i\beta}$.

At defined normal distances from the Gibbs' surface XY, on both its sides, concentrations of the component $i$ in the phases α and β are different from those in the bulk phases, respectively.

The region, in which the changes of the concentration occur, marked in Fig. 7.1 by vertical broken lines, is called ‘the surface or interfacial layer' or ‘the surface phase'.

**Fig. 7.1.** Adsorption at the α and β interface. Real system: solid line – the profile of the concentration changes of component „i” as a function of distance from the XY surface (Gibbs' surface).
b) **Ideal system in which no adsorption takes place (system II)**

A number of moles of the component $i$ in each phase can be calculated as below:

$$n_i^\alpha = V^\alpha c_i^\alpha \quad \text{and} \quad n_i^\beta = V^\beta c_i^\beta \quad (1)$$

where: $V^\alpha$, $V^\beta$ – the volumes of phases $\alpha$ and $\beta$, respectively

---

**Fig. 7.2.** Adsorption at the $\alpha$ and $\beta$ interface.

**Ideal reference system:** broken line shows the concentration profiles of the component $i$ at the changing distance from the Gibbs' surface $XY$. 

c) Comparison of systems I and II

The number of component \( i \) moles that corresponds to the shaded field in Fig. 7.3 is called ‘the surface excess’ and can be calculated from Eq. (2):

\[
\sigma_i = n_i - \left( V^\alpha c_i^\alpha + V^\beta c_i^\beta \right)
\]

where: \( n_i^\sigma \) is the surface excess amount or Gibbs adsorption

In other words, the surface excess is the difference between the amount of a component \( i \) actually present in the system, and that which would be present in a reference system if the bulk concentration in the adjoining phases were maintained up to a chosen geometrical dividing surface; i.e. as though the interface had no effect.

If the area of the dividing surface $XY$ equals $A$ then dividing $n_i^\sigma$ by $A$ the value called surface concentration is obtained, $\Gamma_i^\sigma$.

$$\Gamma_i^\sigma = \frac{n_i^\sigma}{A} \quad (3)$$

Actually, it is excess surface concentration (number of moles per unit area of the dividing surface $XY$) in real system I in relation to the concentration in the ideal system (system II) in which no adsorption of the component $i$ takes place.

Note, the excess concentration may be positive or negative.

The above derivations deal with two component system, a solute and a solution.

For a general case of a multicomponent system Eqs. (3) and (4) can be written:

$$n^\sigma = \sum_i n_i^\sigma \quad \Gamma^\sigma = \sum_i \Gamma_i^\sigma \quad (4)$$

where $n^\sigma$ is the total surface excess and $\Gamma^\sigma$ is the total surface excess concentration.
Gibbs while introducing the dividing surface $XY$ located it in such a way that the surface excess of the principal component (solvent) "1", which is most often water, was zero, $\Gamma_1^{(1)} \equiv 0$.

In other words, the Gibbs' surface $XY$ is in the position that both in the real and reference ideal systems the amount of component 1 is the same.

Then, the excess amount is called 'the relative adsorption of the component $i$'.

Thus, the relative surface excess relates the adsorption at the interface to a solvent in the bulk phase.

An advantage of using the relative surface excess quantities is that they do not depend on the location of the dividing surface.

The relative surface excess $n_i^{\sigma(1)}$ of species $i$ and solvent 1 is therefore expressed (Defay et. al, and Goodrich):

$$n_i^{\sigma(1)} = \left(n_i - c_1^\alpha \ V\right) - \left(n_1 - c_1^\alpha \ V\right) \frac{c_i^\alpha - c_1^\beta}{c_i^\alpha - c_1^\beta}$$  \hspace{1cm} (5)

where $n_1$ and $n_i$ are the total number of moles of component 1 and $i$, respectively, and $V$ is the total volume of the system.
Dividing the relative adsorption by the surface area of the dividing plane $A$, one obtains surface excess concentration of component $i$ in relation to component $1$ (solvent).

$$\Gamma_i^{(1)} = \frac{n_i^{\sigma(1)}}{\sigma}$$

(6)

The areas $1$ and $1'$ on both sides of the dividing surface ($S$) are equal, it means that $\Gamma_i^{(1)} = 0$. However, the areas $2$ and $2'$ differ. The larger one is on the right hand side. Their difference gives the surface excess of the dissolved substance. In this case it is positive, $\Gamma_2^{(1)} > 0$.
Thus the surface excess of component \(i\) defined by Gibbs is the difference between the number of moles of the component on a unit area of the dividing surface (e.g. cm\(^2\)) actually present in the system and that which would be present on the surface in a reference system if the bulk concentration in the adjoining phases were maintained up to a chosen geometrical dividing surface (no adsorption), and in both systems a number of the solvent moles is the same. However, thus defined surface excess is difficult to be understood when the solution concentration is relatively larger.

Therefore Guggenheim and Adam (1933) considered a surface region of thickness \(\tau\) and volume \(V^s\), hence \(V^s = \tau A\). They introduced the concept of 'reduced adsorption of component \(i\)', defined as follows:

\[
\begin{align*}
  n_i^{\sigma(n)} &= n_i^{\sigma} - n^{\sigma} \frac{c_i^\alpha - c_i^\beta}{c^\alpha - c^\beta} \\
  \text{where} \quad c^\alpha &= \sum_i c_i^\alpha \quad \text{and} \quad c^\beta = \sum_i c_i^\beta, \quad n_i^{\sigma} \quad \text{the total number of moles of component \(i\) in the surface region, and} \\
  n^{\sigma} &= \text{the total number of moles of all components present in the surface region.}
\end{align*}
\]
Then reduced surface excess amount $\Gamma_i^{(n)}$ is obtained by dividing $n_i^{\sigma(n)}$ by the interfacial surface area.

$$\Gamma_i^{(n)} = \frac{n_i^{\sigma(n)}}{A}$$

(8)

The reduced surface excess amount does not depend on the location of Gibbs' dividing plane and it can be understood as Gibbs' adsorption of component $i (n_i^{\sigma} \text{ or } \Gamma_i^{\sigma})$ when the $XY$ surface is located in the way that the total surface excess (of all components present in the system) $n^{\sigma} = \sum_i n_i^{\sigma(n)}$ amounts zero. It means that the reference system contains the same total amount of the components ($n$) as the real system.

$$\sum_i n_i^{\sigma(n)} = \sum_i \Gamma^{(n)} = 0$$

(9)
Definitions of **reduced surface excess amounts** $\Gamma_i^{(n)}$, $\Gamma_i^{(m)}$ and $\Gamma_i^{(V)}$ of component $i$:

**Excess $\Gamma_i^{(n)}$**
It is an excess of moles of component $i$ calculated for a unit surface of the interfacial region over **the number of moles** of this component that would be present in the reference system containing **the same total number of moles** as the real system calculated for the unit surface of the interfacial region.

**Excess $\Gamma_i^{(m)}$**
It is an excess of moles of component $i$ calculated for a unit surface of the interfacial region over **the number of moles** of this component that would be present in the reference system containing **the same total mass** as the real system calculated for the unit surface of the interfacial region.

**Excess $\Gamma_i^{(V)}$**
It is an excess of moles of component $i$ calculated for a unit surface of the interfacial region over **the number of moles** of this component that would be present in the reference system containing **the same total volume** calculated for the unit surface of the interfacial region as the real system.
To better understand the definitions we will consider an example.

**Solution**: ethanol in water at the molar ratio $x = 0.5$

**Interface**: solution/air

**Surface region**: of the thickness $\tau$ containing a given amount of the bulk solution.

Assume that the region contains: 10 moles of $\text{H}_2\text{O}$ and 30 moles of $\text{C}_2\text{H}_5\text{OH}$.

**Molecular mass**: water 18 and ethanol 46.

**Molar volume**: water 18 cm$^3$ and ethanol 58 cm$^3$.

### Case 1. $\Gamma_2^{(1)}$

<table>
<thead>
<tr>
<th>surface region is compared with the reference system</th>
<th>surface region</th>
<th>$\text{H}_2\text{O} - 10$ moles</th>
<th>$\text{C}_2\text{H}_5\text{OH} - 30$ moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference system</td>
<td>reference system</td>
<td>$\text{H}_2\text{O} - 10$ moles</td>
<td>$\text{C}_2\text{H}_5\text{OH} - 10$ moles because $x_2 = 0.5$</td>
</tr>
<tr>
<td>excess, n:</td>
<td></td>
<td>0 moles</td>
<td>20 moles</td>
</tr>
</tbody>
</table>

$$
\Gamma_2^{(1)} = \frac{20 \text{ moles}}{A} \\
\text{and} \\
\Gamma_1^{(1)} = \frac{0 \text{ moles}}{A} \\
\text{H}_2\text{O}
$$
### Case 2. $\Gamma_2^{(n)}$

<table>
<thead>
<tr>
<th>surface region is compared with the bulk phase</th>
<th>surface region</th>
<th>$H_2O$ – 10 moles</th>
<th>$C_2H_5OH$ – 30 moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference system</td>
<td>$H_2O$ – 20 moles</td>
<td>$C_2H_5OH$ – 20 moles</td>
<td>because $x_2=0.5$</td>
</tr>
</tbody>
</table>

**excess, n:**

\[
\Gamma_2^{(n)} = \frac{10 \text{ moles}}{A} \quad \text{and} \quad \Gamma_1^{(n)} = -\frac{10 \text{ moles}}{A} \quad H_2O
\]

### Case 3. $\Gamma_2^{(m)}$

<table>
<thead>
<tr>
<th>surface region is compared with the bulk phase</th>
<th>surface region</th>
<th>$H_2O$ – 10 moles</th>
<th>$C_2H_5OH$ – 30 moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference system</td>
<td>$H_2O$ – 24.4 moles</td>
<td>$C_2H_5OH$ – 24.4 moles</td>
<td>1120 g</td>
</tr>
</tbody>
</table>

**excess, n:**

\[
\Gamma_2^{(m)} = \frac{5.6 \text{ moles}}{A} \quad \text{and} \quad \Gamma_1^{(m)} = -\frac{14.4 \text{ moles}}{A} \quad H_2O
\]
## Adsorption at the liquid/gas interface

**Case 4. $\Gamma_2^{(V)}$**

<table>
<thead>
<tr>
<th>surface region is compared with the bulk phase</th>
<th>surface region</th>
<th>( \text{H}_2\text{O} - 10 \text{ moles} )</th>
<th>( 180 \text{ cm}^3 )</th>
<th>( \text{C}_2\text{H}_5\text{OH} - 30 \text{ moles} )</th>
<th>( 1740 \text{ cm}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference system</td>
<td>( \text{H}_2\text{O} - 25.3 \text{ moles} )</td>
<td>( 454 \text{ cm}^3 )</td>
<td>( \text{C}_2\text{H}_5\text{OH} - 25.3 \text{ moles} )</td>
<td>( 1466 \text{ cm}^3 )</td>
<td></td>
</tr>
<tr>
<td>excess, ( n ):</td>
<td></td>
<td>( -15.3 \text{ moles} )</td>
<td>( -274 \text{ cm}^3 )</td>
<td>( +4.7 \text{ moles} )</td>
<td>( +274 \text{ cm}^3 )</td>
</tr>
</tbody>
</table>

\[
\Gamma_2^{(V)} = \frac{4.7 \text{ moles}}{A} \quad \text{and} \quad \Gamma_1^{(V)} = -\frac{15.3 \text{ moles}}{A} \quad \text{H}_2\text{O}
\]

**Comparison of the surface excess values calculated in a different way:**

\[
\Gamma_2^{(1)} = \frac{20 \text{ moles}}{A} > \Gamma_2^{(m)} = \frac{10 \text{ moles}}{A} > \Gamma_2^{(m)} = \frac{5.6 \text{ moles}}{A} > \Gamma_2^{(V)} = \frac{4.7 \text{ moles}}{A}
\]
The above defined surface excess can be expressed by one equation:

\[ \sum_i P_i \Gamma_i = 0 \]  \(10\)

which is called the Guggenheim – Adam's equation.

where:

\[ \Gamma_i^{(n)} \Rightarrow P_i = 1 \]
\[ \Gamma_i^{(m)} \Rightarrow P_i = M_i \]
\[ \Gamma_i^{(V)} \Rightarrow P_i = V_i \]

and: \( M_i \) – the molecular mass of component \( i \),
\( V_i \) – the molar volume of the component.

In the case of a two-component system, the dependence between the Gibbs' and Guggenheim-Adam's surface excesses can be easily derived.

\[ x_1 \Gamma_2^{(1)} = \Gamma_2^{(n)} = \frac{\bar{M}}{M_1} \Gamma_2^{(m)} = \frac{\bar{V}}{V_1} \Gamma_2^{(V)} \]  \(11\)

where \( x_1 \) – the mole fraction of component 1, e.g. water, \( x_2 \) – the mole ratio of component 2, \( \bar{M} = x_1M_1 + x_2M_2 \) – the average molar mass of the solution, \( \bar{V} = x_1V_1 + x_2V_2 \) – the average molar volume of the solution.
If \( x_2 \to 0 \), then: \( x_1, \frac{M}{M_1}, \frac{V}{V_1} \to 1 \) and hence:

\[
\Gamma^{(1)}_2 = \Gamma^{(n)}_2 = \Gamma^{(m)}_2 = \Gamma^{(V)}_2
\]  \tag{12}

For diluted solutions all excesses tend to the same value and change linearly as a function of concentration:

\[
\Gamma_2 = k_2 \times x_2
\]  \tag{13}

Analogical dependence can be derived for the solvent (1).

If \( x_1 \to 0 \), then: \( x_2, \frac{M}{M_1}, \frac{V}{V_1} \to 1 \) then:

\[
\Gamma^{(2)}_1 = \Gamma^{(n)}_1 = \Gamma^{(m)}_1 = \Gamma^{(V)}_1 = k_1 x_1
\]  \tag{14}
Fig. 7.5. Isotherms of surface excess of methanol (component 2) at the aqueous/vapour interface.

These surface excesses were determined by Guggenheim and Adam in 1933.
8. Gibbs' adsorption equation

It deals with the thermodynamic description of solution (α)/gas(β) interface (σ).

For such system we can write the differential:

$$dF = dF^α + dF^β + dF^σ$$

(1)

For changing concentration of component $i$ in the surface layer $σ$ reads:

$$dF = TdS^α + \sum_i \mu_i dn_i^α - p^α dV^α + TdS^β + \sum_i \mu_i dn_i^β - p^β dV^β +$$

$$+ TdS^σ + \sum_i \mu_i dn_i^σ + γdA$$

$$dF^σ = -S^σdT - pdV^σ + γdA + \sum_i \mu_i dn_i^σ$$

(2)

(3)

Because $V^σ \to 0$, the volume of the surface layer, Eq. (3) reduces to Eq. (4).

$$dF^σ = -S^σdT + γdA + \sum_i \mu_i dn_i^σ$$

(4)

When the systems reach the equilibrium, the chemical potential of component $i$ is equal in phases: $α$ (solution), $β$ (gas), and $σ$ (surface layer):

$$\mu_i^α = \mu_i^β = \mu_i^σ = \mu_i$$

(5)
If the equilibrium is reached at $p, T = \text{const}$ then:

$$dF^\sigma = \gamma dA + \sum_i \mu_i d\sigma_i$$  \hspace{1cm} (6)

Integrating this equation from the zero surface to the surface $A$, and the composition of the surface layer does not change we obtain:

$$F^\sigma = \gamma A + \sum_i \mu_i n_i^\sigma$$  \hspace{1cm} (7)

Differentiation of Eq. (7) gives:

$$dF^\sigma = \gamma dA + Ad\gamma + \sum_i \mu_i d\sigma_i + \sum_i n_i^\sigma d\mu_i$$  \hspace{1cm} (8)

Subtraction of Eq. (6) from Eq. (8) leads to Eq. (9).

$$Ad\gamma + \sum_i n_i^\sigma d\mu_i = 0$$  \hspace{1cm} (9)

Or after rearrangement:

$$d\gamma = - \sum_i \frac{n_i^\sigma}{A} d\mu_i$$  \hspace{1cm} (10)

Because $\frac{n_i^\sigma}{A} = \Gamma_i^\sigma$, therefore:

$$d\gamma = - \sum_i \Gamma_i^\sigma d\mu_i$$  \hspace{1cm} (11)

This is the **Gibbs' adsorption equation**.
It relates changes of the solution surface tension $\gamma$ with the surface excess concentration $\Gamma_i^\sigma$ and chemical potential of component $i$. For the two-component system Eq. (11) reads:

$$d\gamma = -\Gamma_1^\sigma d\mu_1 - \Gamma_2^\sigma d\mu_2$$  \hspace{1cm} (12)

For large amount of solvent (1) and low content of solute (2), from the Gibbs approach:

$$\Gamma_1^\sigma = 0 \quad \text{and} \quad d\gamma = -\Gamma_2^{(1)} d\mu_2$$  \hspace{1cm} (13)

Because

$$\mu_2 = \mu_2^o + RT \ln a_2$$  \hspace{1cm} (14)

then

$$d\gamma = -\Gamma_2^{(1)} RT d\ln a_2$$  \hspace{1cm} (15)

From Eqs. (13) and (15)

$$\Gamma_2^{(1)} = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln a_2} \right)_A$$  \hspace{1cm} (16)

$$\Gamma_2^{(1)} = -\frac{a_2}{RT} \left( \frac{\partial \gamma}{\partial a_2} \right)_A$$  \hspace{1cm} (17)

Eqs. (16) and (17) are called the equations of Gibbs' adsorption isotherms.
The equations relate the surface concentration \( \Gamma_2^{(1)} \) with the surface tension changes \( \gamma \) occurring with the changes of component 2 activity \( a_2 \).

For diluted solutions instead of activity \( a_2 \) the component concentration \( c_2 \) can be applied, e.g. mole/dm\(^3\).

\[
\Gamma_2^{(1)} = -\frac{c_2}{RT} \left( \frac{\partial \gamma}{\partial c_2} \right)_A = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c_2} \right)_A
\]

(18)

or

\[
\Gamma_2^{(1)} = -\frac{x_2}{RT} \left( \frac{\partial \gamma}{\partial x_2} \right)_A = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln x_2} \right)_A
\]

(19)

Analogical dependence can be derived for gas adsorption on the liquid surface, e.g. hydrocarbon/water. In such case for water \( d\mu_j = 0 \), hence:

\[
d\gamma = -\Gamma_2^\sigma d\mu_2 \quad (20) \quad \text{then} \quad \Gamma_2^\sigma = -\frac{p_2}{RT} \left( \frac{\partial \gamma}{\partial p_2} \right)_A = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln p_2} \right)_A
\]

(21)
From the Gibbs adsorption isotherm there results:

1. If with the increasing concentration of component 2 (solute), the solution surface tension decreases it means that this surfactant adsorbs on the solution surface because:

\[
\left( \frac{\partial \gamma}{\partial c_2} \right)_A < 0 \quad \text{and} \quad \Gamma_2^{(1)} > 0
\]

positive adsorption

2. If the increasing concentration of component 2 (solute) causes an increase of the solution surface tension it means that it is negative adsorption

\[
\left( \frac{\partial \gamma}{\partial c_2} \right)_A > 0 \quad \text{and} \quad \Gamma_2^{(1)} < 0
\]

negative adsorption

3. If the surface tension of the solution does not change with the increasing concentration of component 2 it means that no adsorption takes place in this system.

\[
\left( \frac{\partial \gamma}{\partial c_2} \right)_A = 0 \quad \text{and} \quad \Gamma_2^{(1)} = 0
\]

no adsorption
Experimental determination of Gibbs adsorption from $\gamma = f(c)$

Fig. 8.1 shows how the Gibbs adsorption can be determined experimentally.

Fig. 8.1. Graphical method for the Gibbs adsorption isotherm $\Gamma = f(c)$ determination from the isotherm $\gamma = f(c)$ by plotting subsequent tangents and calculating tangent values of the angles $\alpha$. 

**Hypotenuse**: (hai'ptuənjuːz) - przeciwprowstokątna

**Leg** - przyległa

**Adjacent** - przeciwprostokątna

**Opposite** - przeciwległa
Experimental determination of Gibbs adsorption from $\gamma = f(c)$  

Adsorption at the liquid/gas interface

**Fig. 8.2.** Graphical method for experimental determination of the Gibbs adsorption $\Gamma = f(c)$ from $\gamma = f(c)$ isotherm using the ordinate sections.

For the calculations of $\Gamma_2^{(1)}$ in mole/m$^2$, the concentration $[c_2] = $ mole/m$^3$, $[\gamma] = $ J/m$^2$, and $R = 8,314$ J/°Kmol should be taken.

Approximate $\Gamma_2^{(1)}$ value can be calculated assuming that:

$$\left(\frac{\partial \gamma}{\partial c_2^i}\right)_A = \left(\frac{\Delta \gamma}{\Delta c_2^i}\right)_A$$
Experimental verification of the Gibbs adsorption equation

1. **Using a mikrotom**, McBain et al. (1932–36) –

   this apparatus allows to 'cut off' a very thin layer (0.05 – 0.1 mm) from the solution surface and then by its analysis the surfactant amount can be determined.

2. **Using radioactive isotopes** of $^{14}\text{C}$, $^{35}\text{S}$ or $^{3}\text{H}$ built in the surfactant molecule one can determine its surface concentration.

3. **Using an ellipsometric method** –

   elliptically polarized light reflected from the solution surface. It allows determination of the surface layer thickness $\tau$ and then $\Gamma$. 
Experimental verification of Gibbs’ equation

1. Using a microtome
McBain et al. (1932–36) used a microtome whose blade moved with velocity over 11 m/s and cut off the surface layer having thickness 0.05 – 0.1 mm, which was then analyzed and the surfactant concentration in the layer was compared with that in the bulk solution.

2. With the help of radioactive tracers
Salley, Dixon et al. used radioactive isotopes, which allowed determination of the concentration change via changes in the radiation intensity if it is not too strong. e.g. $\beta$ of $^{14}$C, $^{35}$S or $^3$H isotopes built in the surfactant molecules. In this way the concentration in the surface layer can be determined.

3. With the help of ellipsometer
Measurement of the reflected polarized elliptically light from the surface allows determination of the surface layer thickness $\tau$, and then $\Gamma$. 

Mikrotom Leica SM 2000 R

Elipsometr M-2000 firmy J.A. Woollam Co.
9. Structure of surface monolayers

Gibbs' monolayers

After dissolution of a surfactant in water, its molecules begin to accumulate (adsorb) at the solution surface until they cover it with a monomolecular layer, commonly called 'monolayer'. The monolayer can be considered as a two-dimensional layer or two-dimensional surfactant film.

Such film demonstrates a pressure $\pi$, called 'the film pressure', which is the difference between the surface tension of a pure liquid and the surface tension of the liquid with a monomolecular layer of a given substance adsorbed on it.

The film pressure is also known as the surface pressure.

$$\pi = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$$ (1)
The film pressure can be measured experimentally and its dimension is mN/m.

Fig. 9.1. Scheme of the set-up for film pressure measurement.

The apparatus for the film pressure measurement is called **Langmuir through** or **Langmuir balance**.

In fact over several decades the authors contributed to its current modern shape, namely: Miss Pockels – Langmuir – Adam – Wilson – McBain (PLAWM).
Adsorption at the liquid/gas interface

From the Gibbs' adsorption equation there follows the dependence:

\[- \frac{d\gamma}{dc} = \Gamma^{(1)}_2 \frac{RT}{c}\]  

(2)

In diluted solutions the interactions between dissolved molecules of the surfactant can be neglected and the solution surface tension will change linearly as a function of the concentration:

\[\pi = \gamma_{\text{solvent}} - \gamma_{\text{solution}}\]

\[\gamma = \gamma_o - bc\]  

(3)

\[\gamma_o - \gamma = bc\]  

(4)

Hence: \[- \frac{d\gamma}{dc} = b\]

and

\[\pi = \Gamma^{(1)}_2 RT\]  

(5)

or

\[\pi A = RT\]  

(6)

where \(A\) is the surface area occupied by one mole of the molecules.

Equation (6) is an equation of state for two-dimensional ideal gas and can be derived from Eq. (5) in the following way.
Equation (6) is an equation of state for two-dimensional ideal gas and can be derived from Eq. (5) in the following way.

Because:

$$\Gamma_2^{(1)} = \frac{n_2^{(1)}}{A}$$  (7)

where $n_2^{(1)}$ – the number of the molecules or moles on the surface $A$

For $n_2^{(1)} = 1$  
$$\Gamma_2 = \frac{1}{A}$$  
therefore  
$$\pi A = RT$$  (6)  (8)

Eq. (8) is an analog of equation of state for an ideal bulk gas $pV = RT$.

If the surfactant solution is more concentrated, for example of an alcohol, a deviation from this linear relationship appears. In such a case Eq. (8) has to be corrected, similarly to the case of real gases.

$$\pi (A - A^\circ) = qRT$$  (9)

where $A^\circ$ is the correction of the total surface for that of the own surface of one mole molecules and $q$ is the correction for the molecules cohesion forces.
The derivative of the surface tension after the concentration \( \left( \frac{\partial \gamma}{\partial c_2} \right)_{c_2 \to 0} \) was called the specific surface activity of the substance (Rebinder). Differentiating the Szyszkowski's equation:

\[
\frac{\gamma_0 - \gamma}{\gamma_0} = B \ln \left( \frac{c_2}{A} + 1 \right)
\]

One obtains:

\[
- \frac{d\gamma}{dc_2} = \frac{B\gamma_0}{c_2 + A}
\]

and introducing into the Gibbs' adsorption the equation \( \left[ \Gamma_2^{(1)} = -\frac{c}{RT} \left( \frac{\partial \gamma}{\partial c} \right)_A \right] \) there results:

\[
\Gamma_2^{(1)} = \frac{B\gamma_0}{RT} \frac{c_2}{c_2 + A}
\]
Adsorption at the liquid/gas interface

If the surfactant is very active then $\Gamma_{2}^{(1)}$ is large already at its low concentration $c_2$, and practically it equals its total amount in the system (component 2). Therefore $\Gamma_2$ can be written without the superscript "1" as expressed in Eq. (13).

\[
\Gamma_{2\infty} = \frac{B\gamma_0}{RT} \Rightarrow \Gamma_2 = \Gamma_{2\infty} \frac{c_2}{c_2 + A}
\]  \hspace{1cm} (13)

where $\Gamma_{2\infty}$ is the complete coverage of the solution surface with the molecules of the surfactant. In such a case $B$ factor is expressed by Eq. (15).

\[
B = \frac{\Gamma_{2\infty} RT}{\gamma_0}
\]  \hspace{1cm} (14)

It appears that for a given homologous series $B$ values are similar. As follows from Eq. (14) magnitude of $B$ depends on the surface area $\omega_m$ occupied by one adsorbed molecule of the surfactant.

\[
\omega_m = \frac{1}{\Gamma_{2\infty} N} = \frac{RT}{B\gamma_0 N}
\]  \hspace{1cm} (15)

Where $N$ is the Avogadro number. Thus the calculated values of $\omega_m = RT/B\gamma_0 N$ are in the range of 0.2–0.4 nm$^2$. 
It follows from the Traube's rule that the surface activity depends upon the chain length and the work needed to transport one mole of the surfactant molecules from the bulk solution to its surface $W_s$ is expressed:

$$W^s = RT \ln \frac{c^s}{c} \quad (16)$$

where $c$ is the bulk phase concentration and $c_s$ is that on the surface. If the chain length is increased from $n$ to $n + 1$ C atoms, the work will also increase:

$$W_{n+1}^s - W_n^s = RT \ln \frac{c_{n+1}^s \cdot c_n}{c_n^s \cdot c_{n+1}} \quad (17)$$

If the chain lengths ratio equals 3.2 then the surface concentration of both surfactants has to be the same, $c_n^1 = c_{n+1}^1$ and at 293°C the difference in the work is:

$$W_{n+1}^s - W_n^s = RT \ln 3.2 = 2930 \text{ } \text{J/mol} \quad (18)$$
The difference stands for the work of 1 mole of $-\text{CH}_2-$ groups transportation from the bulk solution to its surface. Its value does not depend on the chain length and one can conclude that all $-\text{CH}_2-$ on the surface are arranged in the same way, that is they lie flat, which is possible in the case of a diluted solution, when even apolar $-\text{CH}_2-$ groups interact more strongly with water than with the gas phase. With the increasing concentration of the surfactant, the number of its molecules on the surface increases. They start to reorient from lying flat to standing and finally are closely packed like a brush. This is depicted in Fig. 9.2.

**Fig. 9.2.** A scheme of surfactant molecules structure at the solution/gas interface: a) diluted solution, b) more concentrated, c) completely covered surface.
10. Insoluble films on liquid surface

Such films are formed when several droplets of an insoluble organic substance dissolved in an organic volatile solvent (e.g. chloroform) are spread on the liquid (water or an aqueous solution, so called subphase). Then the solvent evaporates leaving the substance film spread. Nowadays these films are called Langmuir films.

Historical background

[http://en.wikipedia.org/wiki/Langmuir%E2%80%93Blodgett_film#Historical_background]

⇒ Advances to the discovery Langmuir-Blodgett Films began with Benjamin Franklin in 1773 when he dropped about a teaspoon of oil onto a pond. Franklin noticed that the waves were calmed almost instantly and that the calming of the waves spread for about half an acre (1 Acre = 0.4 ha). What Franklin did not realize was that the oil had formed a monolayer on top of the pond surface.
Formation of monomolecular layers is a spontaneous process due to so called *hydrophobic effect*

Monolayer of amphifilic molecules: (a) two-dimensional gas, and (b) In condensed state, on the surface of subphase in Langmuir trough.
Benjamin Franklin (January 17, 1706–April 17, 1790) was one of the Founding Fathers of the United States. A noted polymath, Franklin was a leading author, printer, political theorist, politician, postmaster, scientist, musician, inventor, satirist, civic activist, statesman, and diplomat. As a scientist, he was a major figure in the American Enlightenment and the history of physics for his discoveries and theories regarding electricity. He invented the lightning rod, bifocals, the Franklin stove, a carriage odometer, and the glass 'armonica'. He facilitated many civic organizations, including a fire department and a university.

Franklin's birthplace site directly across from Old South Meeting House on Milk Street is commemorated by a bust above the second floor facade of this building.
Historical background
[http://en.wikipedia.org/wiki/Langmuir%E2%80%93Blodgett_film#Historical_background]

⇒ Over a century later, **Lord Rayleigh** quantified what **Benjamin Franklin** had seen at a pond. Knowing that the oil, oleic acid, had spread evenly through water, then Lord Rayleigh calculated that the thickness of the film was 1.6 nm by knowing the volume of oil dropped and the area of coverage. In addition, he used these calculations to prove Avogadro’s number.
Historical background
[http://en.wikipedia.org/wiki/Langmuir%E2%80%93Blodgett_film#Historical_background]

With the help of her kitchen sink, Agnes Pockels showed that area of films can be controlled with barriers. She added that surface tension varies with contamination of water. She used different oils to deduce that surface pressure would not change until area was confined to about 0.2 nm² (so called Pockels' point). This work was originally written as a letter to Lord Rayleigh who then helped Agnes Pockels to published it in the journal, Nature, in 1891.
Agnes Pockels work set the stage for Irving Langmuir who continued to work and confirmed Pockels’ results. Using Pockels’ idea, he developed the Langmuir trough. His observations indicated that chain length did not impact the affected area since the organic molecules were arranged vertically.
Historical background
[http://en.wikipedia.org/wiki/Langmuir%E2%80%93Blodgett_film#Historical_background]

Langmuir’s breakthrough (punkt zwrotny) did not occur until he hired Katherine Blodgett as his assistant. Blodgett initially went to seek for a job at General Electric (GE) with Langmuir during her Christmas break of her senior year at Bryn Mawr College, where she received at BA in Physics. Langmuir advised to Blodgett that she should continue her education before working for him. She thereafter attended University of Chicago for MA in Chemistry. Upon her completion of her Masters, Langmuir hired her as his assistant.
Historical background
[http://en.wikipedia.org/wiki/Langmuir%E2%80%93Blodgett_film#Historical_background]

However, breakthroughs in surface chemistry happened after she received her PhD degree in 1926 from Cambridge University. While working for GE, Langmuir and Blodgett discovered that when a solid surface is inserted into an aqueous solution containing monolayers of organics then the monolayer will deposit homogeneously over the surface. This process created Langmuir-Blodgett Films. Through this work in surface chemistry and with the help of Blodgett, Langmuir was awarded the Nobel Prize in 1932. In addition, Blodgett applied the Langmuir-Blodgett Film principle to create 99% transparent anti-reflective glass by coating glass fluorine containing organics.
Fig. 10.1 shows modern **Langmuir-Blodgett trough** used for surface films investigations.

**Fig. 10.1.** A) Modern automated Langmuir-Blodgett trough KSV 2000 (KSV Instruments Ltd., Finland), B) Surface pressure measurement by a Wilhelmy plate.
Compressing the film with the help of the barrier the molecules laying flat on the surface come closer until they become packed touching each other (Pockels' point).

The free energy of the film is thus increased and it will tend to increase its surface. Langmuir found that the area per molecule in Pockels point was the same for:
- palmitic acid (hexadecanoic acid) $\text{C}_{15}\text{H}_{31}\text{COOH}$,
- stearic acid (octadecanoic acid) $\text{C}_{17}\text{H}_{35}\text{COOH}$,
- keratin acid (hexacosanoic acid) $\text{C}_{25}\text{H}_{51}\text{COOH}$,

and amounted $21 \text{Å}^2$/molecule ($0.21 \text{nm}^2$/molecule).

Because the chain length increased and the surface per molecule did not change, it proved that the molecules were oriented vertically when compressed to the Pockels point.

The investigations of the films were developed very much during interwar years. They were conducted by outstanding scientists, like Langmuir, Adam, Harkins, Readel.

It is worth to mention that the surface of seas and lakes is in fact covered with natural films whose principal components are glycoproteins.
The following types of such films can be distinguished:

- film – generally a thin layer deposited on a liquid (or solid) surface,
- monomolecular film – one molecule thick film,
- bilayer film – two molecule thick film,
- duplex film – thick film whose the two surfaces possesses different properties, especially the surface tension,
- liquid lens of insoluble liquid drop placed on surface of other liquid. It means that this former liquid does not spread onto the surface of later one.
Thermodynamic criterion for spreading of a liquid over another immiscible liquid

The change of thermodynamic potential $G$ due to the liquid spreading can be expressed as total differential $dG$, as expressed by Eq. (1).

$$dG = \frac{\partial G}{\partial A_A} dA_A + \frac{\partial G}{\partial A_{AB}} dA_{AB} + \frac{\partial G}{\partial A_B} dA_B$$  \hspace{1cm} (1)

Fig. 10.2. Spreading of liquid $B$ over surface of liquid $A$.

However, there is relationship between the liquids surface area changes:

$$dA_B = -dA_A = dA_{AB}$$  \hspace{1cm} (2)
The increase of liquid $B$ surface corresponds to simultaneous decrease of liquid $A$ surface by the same amount, and increase of interfacial surface $AB$.

But: \[
\frac{\partial G}{\partial A_A} = \gamma_A; \quad \frac{\partial G}{\partial A_B} = \gamma_B; \quad \frac{\partial G}{\partial A_{AB}} = \gamma_{AB}
\] (3)

**Fig. 10.2.** Spreading of liquid $B$ over surface of liquid $A$.

\[
S_{B/A} = W_{BA}^{spr} = \gamma_A - \gamma_B - \gamma_{AB}
\] (4)

If $W_{BA}^{spr} = S_{BA} > 0$, then liquid $B$ spreads over surface of liquid $A$.

\[
W_{BA}^{spr} = W_{BA}^{adh} - W_{BB}^{koh}
\] (5)

It should be kept in mind that the two liquids may partially mutually dissolved, which affects the liquids surface tension and the interfacial tension.
An example is system benzene-on-water.

Putting of a drop of benzene on the surface of water initially benzene is not dissolved.

Surface and interfacial tensions:
- water/air: 72.8 mN/m
- benzene/air: 28.9 mN/m
- benzene/water: 35.0 mN/m

\[ W_{spr} = 72.8 - 28.9 - 35.0 = +8.9 > 0 \rightarrow \text{benzene spreads on water.} \]

After a short while some benzene from the spreading drop dissolves in the water, but water in the benzene practically does not dissolve. It causes the water/air surface tension drops to 62.4 mN/m.

Now \[ W_{spr} = 62.2 - 28.8 - 35.0 = -1.6 < 0 \]

the spreading stops, and the oil retracts to a lens.
Isotherms of film pressure $\pi$ versus surface area $A$ per molecule

On the compression the film may undergo several phase transition. Further compression of the film, when it is in a solid-like state; causes it folding, then breaking, and collapse.

**Fig. 10.3.** Different states of Langmuir films
(From A.W. Adamson, Physical Chemistry of Surfaces)

**Fig. 10.4.** Different states of the cholesterol Langmuir films
Adsorption at the liquid/gas interface

Langmuir-Blodgett method

Langmuir-Schaefer method


Qiang He, Junbai Li, Adv. in Colloid and Interface Science 131 (2007) 91-98

Pressure/area diagram of a lipid monolayer: representation of the compression behavior and packing in the gasous (G), liquid-expanded (LE), liquid-condensed (LC), and solid (S) phases

Fig. 10.7. Schematic representation of Langmuir-Blodgett and Langmuir-Schaefer methods for solid-supported film formation and pressure/area diagram of different film states.
States of the Langmuir films

**Gaseous films (G)** – they obey equation of state for ideal gas. The surface area per molecule is much larger than the molecule size. The film pressure very low, less than 0.01 mN/m.

**Liquid films (L)** – relatively compact, weak intermolecular interactions are present, they are fluidic films among which can be distinguished:

- **liquid expended (L₁)** – (Adam and Harkins), extrapolated to zero the film pressure $\pi$ gives the surface per molecule $A = 50 \, \text{Å}^2$ (see Fig. 10.3), their compressibility is bigger than that of the appropriate liquid;

- **liquid condensed (L₂)** – their polar heads are closely packed, they rearrange upon compression. They may oppose their compression and a lower temperature may convert themselves to $L₁$ and then to gaseous $G$. On the other hand, their compression can convert them into solid-like films with 0.22 nm$^2$/molecule ($22 \, \text{Å}^2$/molecule). Such behavior is characteristic for cetyl alcohol (1-hexadecanol) films $C_{16}H_{33}OH$. 
States of the Langmuir films

**Solid films (S)** – they show linear $\pi - A$ dependence (e.g. fatty acids on water).

The film pressure extrapolated to zero value corresponds the surface area per molecule $0.205 \text{ nm}^2 (20.5 \text{ Å}^2)$, which indicates for closely packed hydrocarbon chains that show rigidity. At a lower pressures the film can brake (curve f on the figure) and convert to $L_2$ film. Further compression of the solid film may result in the film collapse and formation of the second layer.

The above classification of the film structures are model ones and in real systems their structures may be more complicated.

Fig. 10.5 shows scheme of the film collapse and electron microscope picture of the collapsed film.
The film structure may depend on pH which can influence ionization of the polar groups of the molecules forming the film and appearing of repulsive forces that can cause change in the film structure, for example from solid to liquid or even gaseous. Also presence of ions in the aqueous subphase can affect the film structure, e.g. soap formation.
Films of organic substances

These are very important films for living organisms. The films are formed by proteins, steroids, lipids and others.
In Fig. 10.6 is shown structure of oriented phospholipid (lecithin) molecule on water surface, and Fig. 10.7 presents $\pi$ - $A$ isotherms, which are similar to those of fatty acids.

Fig. 10.5. Model of lecithin molecule.

Fig. 10.6. Isotherms of $\pi$-A changes of lipids.
Investigations of organic films, and polymers, not only on water and aqueous solutions but also on other liquids, including mercury, are broadly carried out. The films can be also obtained in bulk phase of water. They are formed of a lipid spread on a frame. At their thickness 6 – 9 nm (60 – 90 Å) such films become black.

**Langmuir–Blodgett films**

These are films deposited on a solid substrate, like glass, silicon, mica, gold, e.t.c. They are obtained by transferring the Langmuir film from liquid surface onto a solid one. This can be done using Longmuir-Blodgett trough (Fig. 10.1) by withdrawing the solid plate from beneath the film present on the liquid surface in the trough.

This process can be repeated several times. If for example glass plate is withdrawn through barium stearate \((C_{17}H_{35}COO)_2Ba\) the glass surface becomes hydrophobic. However, if the plate with the first layer is withdrawn for the second time its surface now becomes hydrophilic. This method is called Langmuir–Blodgett method.
The second monolayer can be also formed by touching the plate parallel to the film. This is **Langmuir-Schafer method**. Depending on the kind of the Langmuir film it is possible to deposit as many as up to one hundred monolayers, which can be disordered inside such a thick film. The methods of the film transferring are depicted in Fig. 10.7.
Langmuir-Blodgett and Langmuira-Schaefera methods

Langmuir-Blogett method

Langmuir-Schaefera method
Solid substrates in LB films

Kind of substrate:

**Hydrophilic:**
- plates of glass and quartz
- plates of Cr, Al, Sn oxides
- plates of silver and gold (current conducting substrates)
- plates of Si and GaAs (semiconducting substrates)

**Hydrophobic:**
- highly oriented pyrolitic graphite (HOPG)
Bilayers and Vesicles

Biological cell membranes are formed of bilayers which consists of two monolayers, mostly of lipids, phospholipids and proteins, directed with their hydrocarbon chains inward and polar heads outward the bilayer. Its thickness is about 5 nm. A model of such bilayer membrane is shown in Fig. 10.8 and 10.9.

A successful model of membrane structure is that of fluid mosaic, where the proteins are ‘icebergs’ in the ‘lipid sea’.


Fig. 10.8. Model of biological membrane.
Bilayers and Vesicles

While affected by ultrasounds they can form spherical structures called **vesicles**, or **liposomes** having dimensions from 1 nm up to 100 nm. They can include water molecules inside the structure.

**Fig. 10.9.** Bilayers of lecithin, a) „twist”, b) splay.

CMC of phospholipids is very low, for example $4.7 \cdot 10^{-7}$ M for synthetic lecithin.
The liposomes can also form spontaneously from phospholipids in which the polar heads are directed outward and hydrophobic tails inward, as is shown in the figure below.

Structure of liposome

Nowadays bilayers and vesicles are very intensively investigated with the help of advanced spectroscopic and microscopic techniques that allow for learning about their structures almost on a molecular level.