Lecture 2

Adsorption and the thermodynamics of surfaces

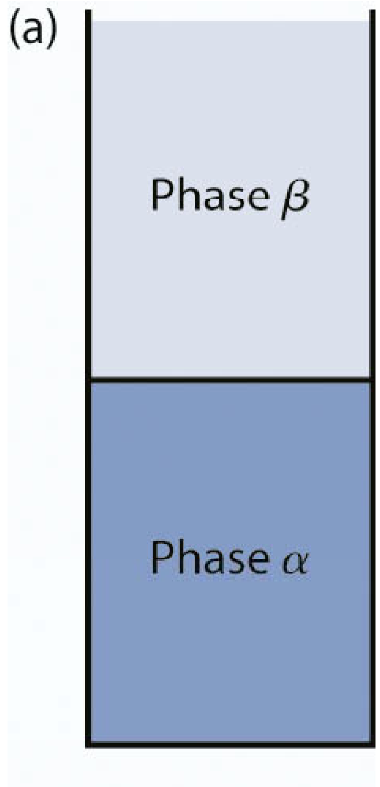
Adsorption at gas liquid interface

Adsorption

- Adsorption - a tendency of one component to have a higher or lower concentration at the interface in comparison to adjacent phase.

Models of the interface

- A system containing an interface can be divided into 3 regions



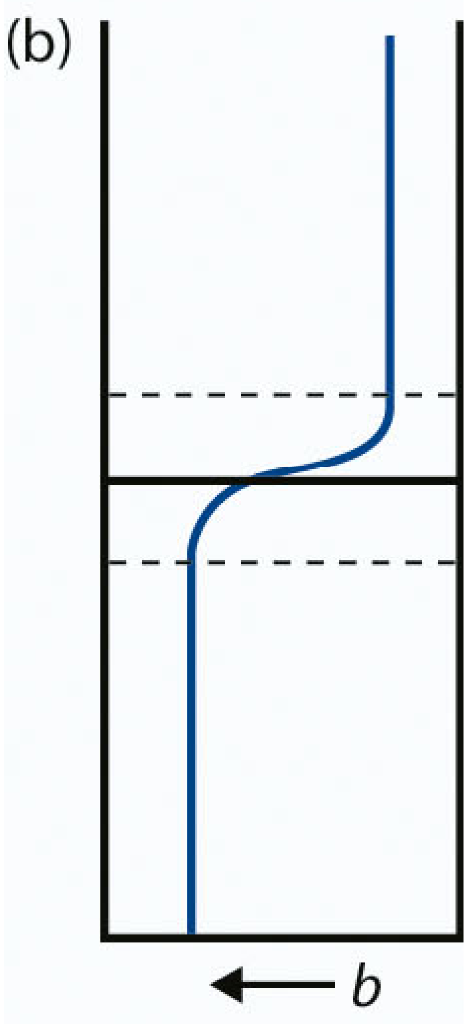
for an extensive property B:

$$B = B^{\alpha} + B^{\beta} + B^{\sigma}$$

Models of the interface

1. Surface phase approach (Guggenheim)

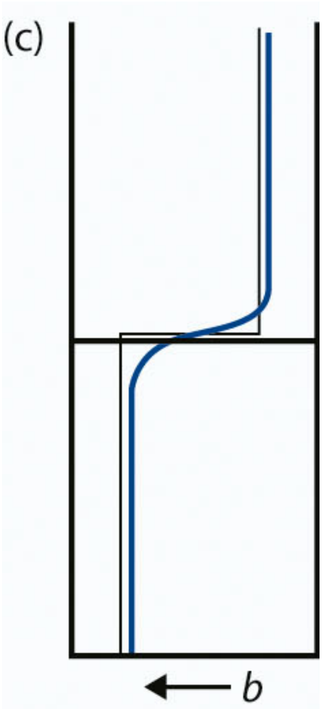
- interfacial region has finite thickness;
- properties in the bulk phases are uniform



Models of the interface

2. Surface excess properties approach (Gibbs)

- interface is infinitely thin;
- properties of bulk phases assumed to extend till the interface;
- difference between the real property B and the model value is called **excess**



extensive property: $$B_{\text{excess}} = B^{\sigma} = B_{\text{real}} - B_{\text{model}}$$

$$V = V^{\alpha} + V^{\beta}, \quad V^{\sigma} = 0$$

intensive property: $$b = B / V$$

Example: **concentration** $$n_{i,\text{model}} = c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta}$$

excess $$n_i^{\sigma} = n_i - \left(c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta} \right)$$

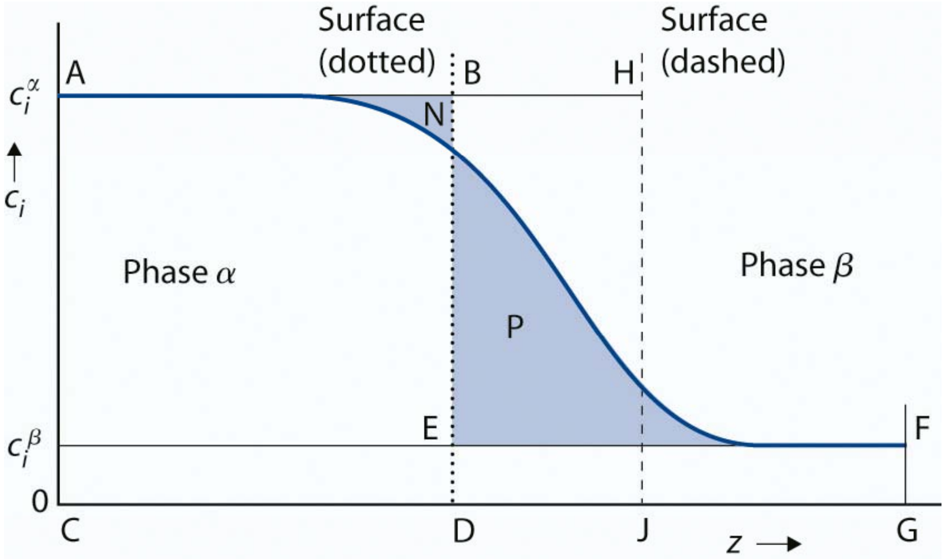
Adsorption

surface excess:

$$n_i^{\sigma} = n_i - \left(c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta}\right)$$

$$\Gamma_i = n_i^{\sigma} / A$$

adsorption



- the value of adsorption depends of the interface position! so, we need to agree on a convention….

<u>Gibbs convention:</u>

- adsorption of a major component is zero:

$$\Gamma_A = n_A^{\sigma} / A = 0$$

Adsorption

- relative adsorption

$$n_i^{\sigma} = n_i - \left(c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta}\right) = n_i - c_i^{\alpha} V + \left(c_i^{\alpha} - c_i^{\beta}\right) V^{\beta}$$

$$n_A^{\sigma} = n_A - c_A^{\alpha} V + \left(c_A^{\alpha} - c_A^{\beta}\right) V^{\beta}$$

in the combination below V^{b} will be eliminated:

$$n_i^{\sigma} - n_A^{\sigma}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_A^{\alpha} - c_A^{\beta}}\right) = n_i - c_i^{\alpha} V - \left(n_A - c_A^{\alpha} V\right)\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_A^{\alpha} - c_A^{\beta}}\right)$$

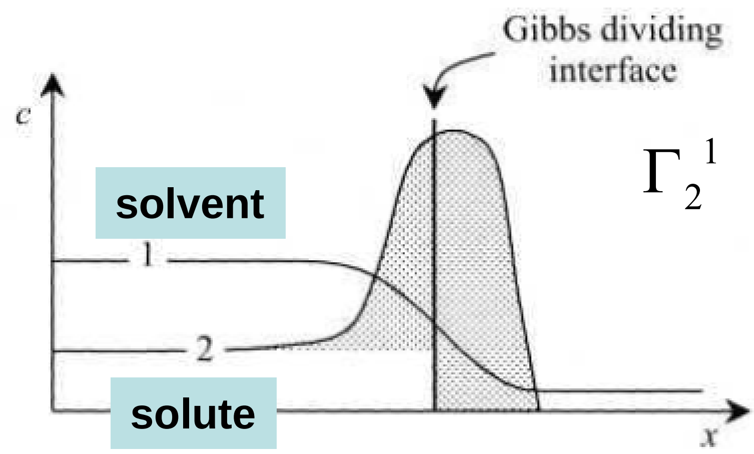
doesn’t depend on interface position!

normalizing this by area will make **relative adsorption**

$$\Gamma_i^{A} = \Gamma_i - \Gamma_A \frac{c_i^{\alpha} - c_i^{\beta}}{c_A^{\alpha} - c_A^{\beta}}$$

Adsorption

$$\Gamma_i^A = \Gamma_i - \Gamma_A \frac{c_i^\alpha - c_i^\beta}{c_A^\alpha - c_A^\beta}$$



- **Gibbs convention:**

$$\Gamma_A = 0, \ \Gamma_i^A = \Gamma_i (Gibbs)$$

- The relative adsorption of ***i*** with respect to A is equal to the adsorption of ***i*** using Gibbs convention

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- **adsorption isotherm**: dependence of the adsorption vs. bulk concentration at constant temperature. Adsorption isotherm is described by an **isotherm equation**

Thermodynamic properties of interfaces

- Consider a system of two phases separated by an interface
- Let's start with the internal energy as it only contains extensive quantities as variables:

Generally: $$dU = \delta q + \delta w = TdS - PdV + \sum_i \mu_i dn_i$$

Sum over all components present in the system

$$dU = dU^{\alpha} + dU^{\beta} + dU^{\sigma}$$

$$dU = TdS^{\alpha} - P^{\alpha} dV^{\alpha} + \sum_i \mu_i^{\alpha} dN_i^{\alpha}$$

$$TdS^{\beta} - P^{\beta} dV^{\beta} + \sum_i \mu_i^{\beta} dN_i^{\beta}$$

$$TdS^{\sigma} + \gamma dA + \sum_i \mu_i^{\sigma} dN_i^{\sigma}$$

As the interface is infinitely thin, it cannot perform volume work.

Thermodynamic properties of interfaces

- Rearranging:

$$dU = TdS - P^{\alpha} dV - \left(P^{\beta} - P^{\alpha}\right) dV^{\beta} + \sum_i \mu_i^{\alpha} dN_i^{\alpha} + \sum_i \mu_i^{\beta} dN_i^{\beta} + \sum_i \mu_i^{\sigma} dN_i^{\sigma} + \gamma dA$$

- for Helmholtz energy:

$$dF = -SdT - P^{\alpha} dV - \left(P^{\beta} - P^{\alpha}\right) dV^{\beta} + \sum_i \mu_i^{\alpha} dN_i^{\alpha} + \sum_i \mu_i^{\beta} dN_i^{\beta} + \sum_i \mu_i^{\sigma} dN_i^{\sigma} + \gamma dA$$

=0 at
T, V = constant.

- in a closed system: $dN_i^{\sigma} = -\left(dN_i^{\alpha} + dN_i^{\beta}\right)$

$$\frac{dF}{dN_i^{\alpha}} = \mu_i^{\alpha} - \mu_i^{\sigma} = 0; \quad \frac{dF}{dN_i^{\beta}} = \mu_i^{\beta} - \mu_i^{\sigma} = 0$$

$$dF = \left(P^{\beta} - P^{\alpha}\right) dV^{\beta} + \gamma dA; \quad \left.\frac{\partial F}{\partial A}\right|_{T,V,V^{\beta},N_i} = \gamma$$

Thermodynamic properties of interfaces

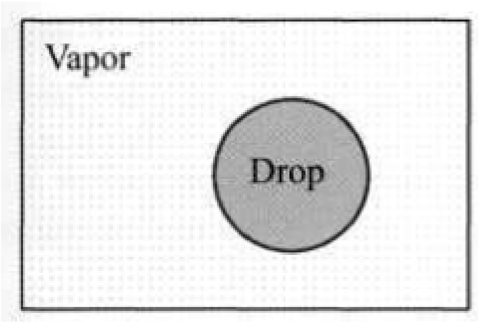
- Young-Laplace equation:

$$dF = -\left(P^{\beta} - P^{\alpha}\right) dV^{\beta} + \gamma dA;$$

$$\frac{dF}{dA} = \frac{\partial F}{\partial A} + \frac{\partial F}{\partial V^{\beta}} \frac{\partial V^{\beta}}{\partial A} = \gamma - \left(P^{\beta} - P^{\alpha}\right)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1} = 0$$

- For a case of a spherical droplet:

$$P^{\beta} - P^{\alpha} = 2\gamma/r = 2\gamma'/r'$$



Surface tension depends on the location of Gibbs plane in a case of curved interface! No such problems on a planar interface...

Thermodynamic properties of interfaces

- Similarly for Gibbs free energy:

$$dG = -SdT + V^{\alpha} dP^{\alpha} + V^{\beta} dP^{\beta} + \gamma dA + \sum_i \mu_i dn_i$$

- in a case of planar interface:

$$dG = -SdT + VdP + \gamma dA + \sum_i \mu_i dn_i$$

$$\left.\frac{\partial G}{\partial A}\right|_{T,P,N_i} = \gamma$$

- at constant temperature we can integrate the surface term and normalize it by the area

$$\frac{G^{\sigma}}{A} = \gamma + \sum_i \mu_i^{\sigma} d\Gamma_i^{\ \sigma}$$

$$\frac{U^{\sigma}}{A} = \frac{H^{\sigma}}{A} = \frac{TS^{\sigma}}{A} + \gamma + \sum_i \mu_i^{\sigma} d\Gamma_i^{\ \sigma}$$

Thermodynamic properties of interfaces

- Surface excess of thermodynamic functions:

$$dU^\sigma = TdS^\sigma + \gamma dA + \sum_i \mu_i dN_i^\sigma$$

$$dF^\sigma = -S^\sigma dT + \gamma dA + \sum_i \mu_i dN_i^\sigma$$

- As U is a linear homogeneous function:

$$U^\sigma = TS^\sigma + \gamma A + \sum_i \mu_i N_i^\sigma$$

$$F^\sigma = U^\sigma - TS^\sigma = \gamma A + \sum_i \mu_i N_i^\sigma$$

- in a case of planar interface:

- entropy-surface tension relation:

Maxwell relations for exact differential:

$$f = gdx + hdy \Rightarrow \left.\frac{\partial g}{\partial y}\right|_x = \left.\frac{\partial h}{\partial x}\right|_y$$

$$-\left.\frac{\partial S^\sigma}{\partial A}\right|_{T,N_i} = \left.\frac{\partial \gamma}{\partial T}\right|_{A,N_i} \Rightarrow \quad s^\sigma = -\left.\frac{\partial \gamma}{\partial T}\right|_{A,N_i} \quad u^\sigma = \gamma - T\left.\frac{\partial \gamma}{\partial T}\right|_{A,P} ; \; q = -T\frac{\partial \gamma}{\partial T}$$

heat per unit area

Gibbs adsorption isotherm

- Let's consider internal energy:

$$dU^{\sigma} = TdS^{\sigma} + \gamma dA + \sum_i \mu_i dN_i^{\sigma}$$

$$U^{\sigma} = TS^{\sigma} + \gamma A + \sum_i \mu_i N_i^{\sigma}$$

- Gibbs-Duhem equation:

$$S^{\sigma} dT + Ad\gamma + \sum_i N_i^{\sigma} d\mu_i = 0$$

- at constant temperature:

$$d\gamma = -\sum_i \Gamma_i^{\sigma} d\mu_i$$

Gibbs Adsorption Isotherm

- for 2-component mixture:

$$\Gamma_2^{(1)} = -\frac{1}{RT}\frac{d\gamma}{d(\ln a)} = -\frac{a}{RT}\frac{d\gamma}{da}$$

if $\Gamma>0$ $d\gamma/da<0$
if $\Gamma<0$ $d\gamma/da>0$

Marangoni effect

- Tears of wine

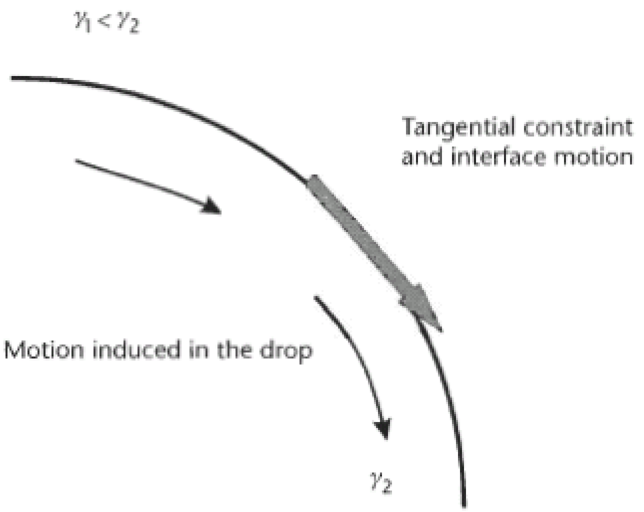
Marangoni effect

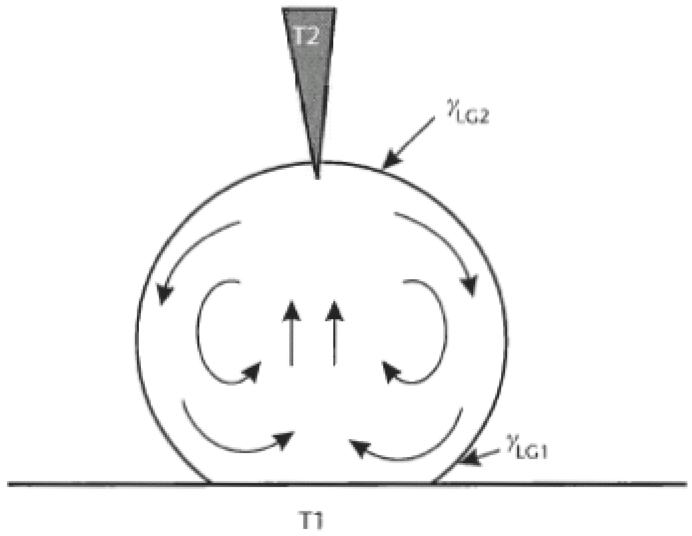
- surface tension depends on temperature as

$$\gamma = \gamma_0 (1 - \beta (T - T_0))$$

for water/air interface: γ_0=72mN/m and β=0.1 mN/(m K)

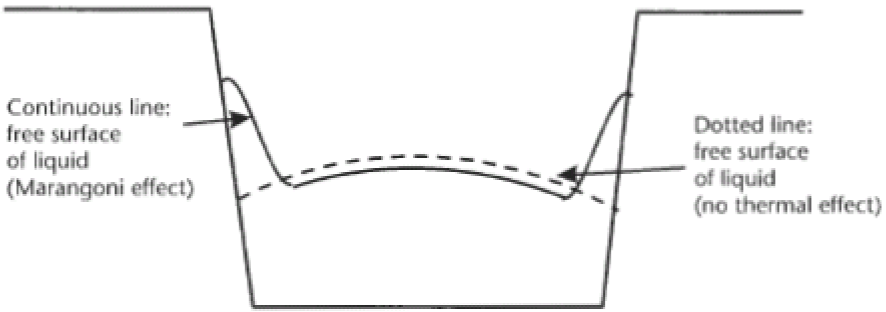
- surface tension distribution induces tangential force distribution on the interface and convective motion inside the droplet



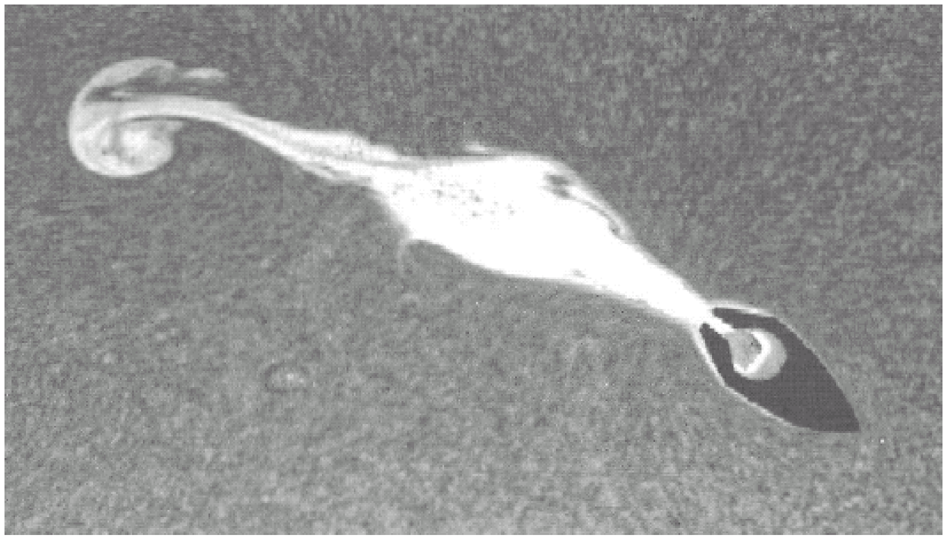


Marangoni effect

- Marangoni effect due to temperature in a microwell



- Marangoni effect due to surfactant concentration



Measurement of adsorption

Methods for measuring adsorption can be grouped into following categories

- adsorption from concentration change

$$n_i^{\sigma} = n_i^0 - n_i = \left(c_i^0 - c_i\right)V$$

- adsorption from surface analysis (sampling at the surface)

$$n_{i,real} = c_i^L V^L + c_i^S V^S + c_i^G V^G$$

$$n_i^{\sigma} = n_{i,real} - n_{i,\mathrm{model}} = \left(c_i^S - c_i^L\right)V^S$$

- adsorption from surface tension change

Gibbs equation:

$$\frac{-d\gamma}{RT} = \sum_i \left(\Gamma_i d\ln(a_i)\right)$$

for 2 component system:

$$\Gamma_B = \frac{a_B}{RT}\frac{d\gamma}{d(a_B)}$$

Measurement of adsorption

- adsorption from concentration change

$$n_i^{\sigma} = n_i^{0} - n_i = \left(c_i^{0} - c_i\right)V$$

- adsorption from surface analysis (sampling at the surface)

$$n_{i,real} = c_i^{L}V^{L} + c_i^{S}V^{S} + c_i^{G}V^{G}$$

$$n_i^{\sigma} = n_{i,real} - n_{i,\mathrm{model}} = \left(c_i^{S} - c_i^{L}\right)V^{S}$$

- adsorption from surface tension change

Gibbs equation: $$\frac{-d\gamma}{RT} = \sum_i \left(\Gamma_i d\ln(a_i)\right)$$

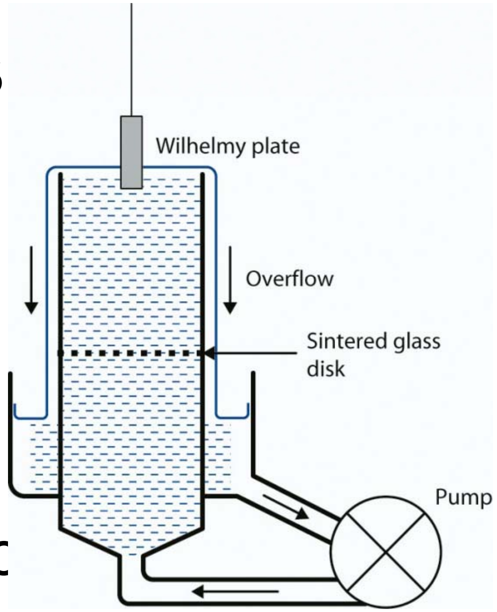
for 2 component system: $$\Gamma_B = \frac{a_B}{RT}\frac{d\gamma}{d(a_B)}$$

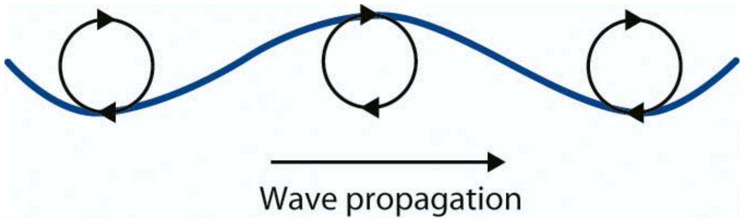
Adsorption at Gas-Liquid interface

- Measurements of equilibrium adsorption
  - surface tension measurements (Wilhelmy plate)
  - surface analysis
    - radio-labelled solutes
    - neutron reflectometry (deuterated solutes)
    - X-ray reflectometry
    - formation and collection of foam

Adsorption at Gas-Liquid interface

- Observation of adsorption kinetics
  - adsorption at freshly formed interfaces
  - surface waves:
    - transverse capillary waves (ripples generated by an oscillating hydrophobic knife edge, f=100-300 Hz). Energy dissipation caused by compression-expansion cycle.
    - longitudinal waves (horizontal movement of barrier, <0.1 Hz)





Adsorption of non-electrolyte solutes

- Negative adsorption

  observed in dilute aqueous solutions of e.g. glycine and sucrose

- Kinetics of adsorbtion

  in case of no stirring and no energy barrier:

$$\frac{d\Gamma}{dt} = \left(\frac{D}{\pi}\right)^{1/2} c t^{-1/2}, \quad \Gamma = 2ct\left(\frac{D}{\pi}\right)^{1/2}$$

Adsorption of ionized solute

- in case ionized solute the Gibbs equation must include contribution of all ions:

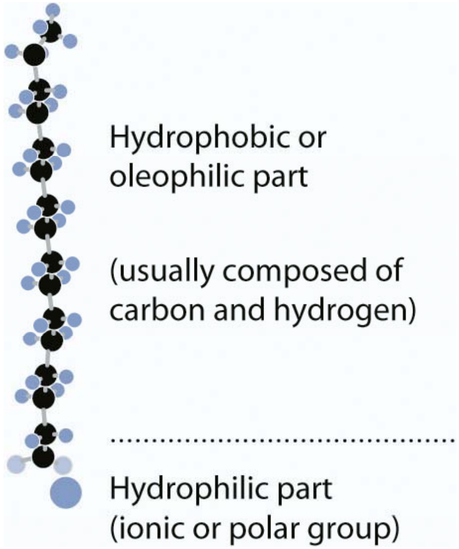
$$\frac{-d\gamma}{RT} = \Gamma_{M^+} d\ln c_{M^+} + \Gamma_{X^-} d\ln c_{X^-}$$

from electro neutrality: $c_{M^+} = c_{X^-} = c$ and $\Gamma_{M^+} = \Gamma_{X^-} = \Gamma$

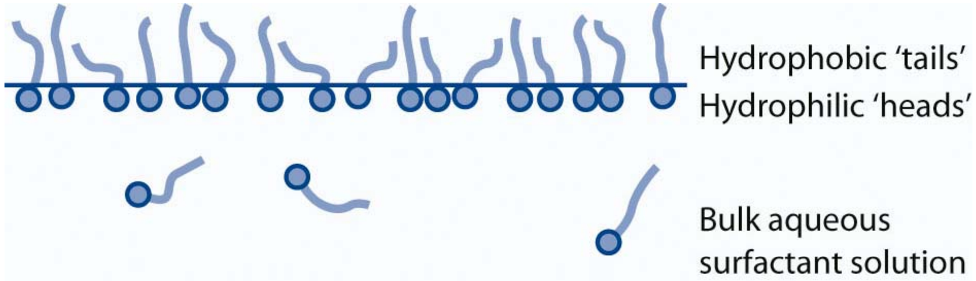
$$\Gamma = \frac{1}{2RT}\frac{-d\gamma}{dc}$$

Absorption of surfactants

- **surfactants** (stands for: surface active agents) belong to a class of **amphiphiles**

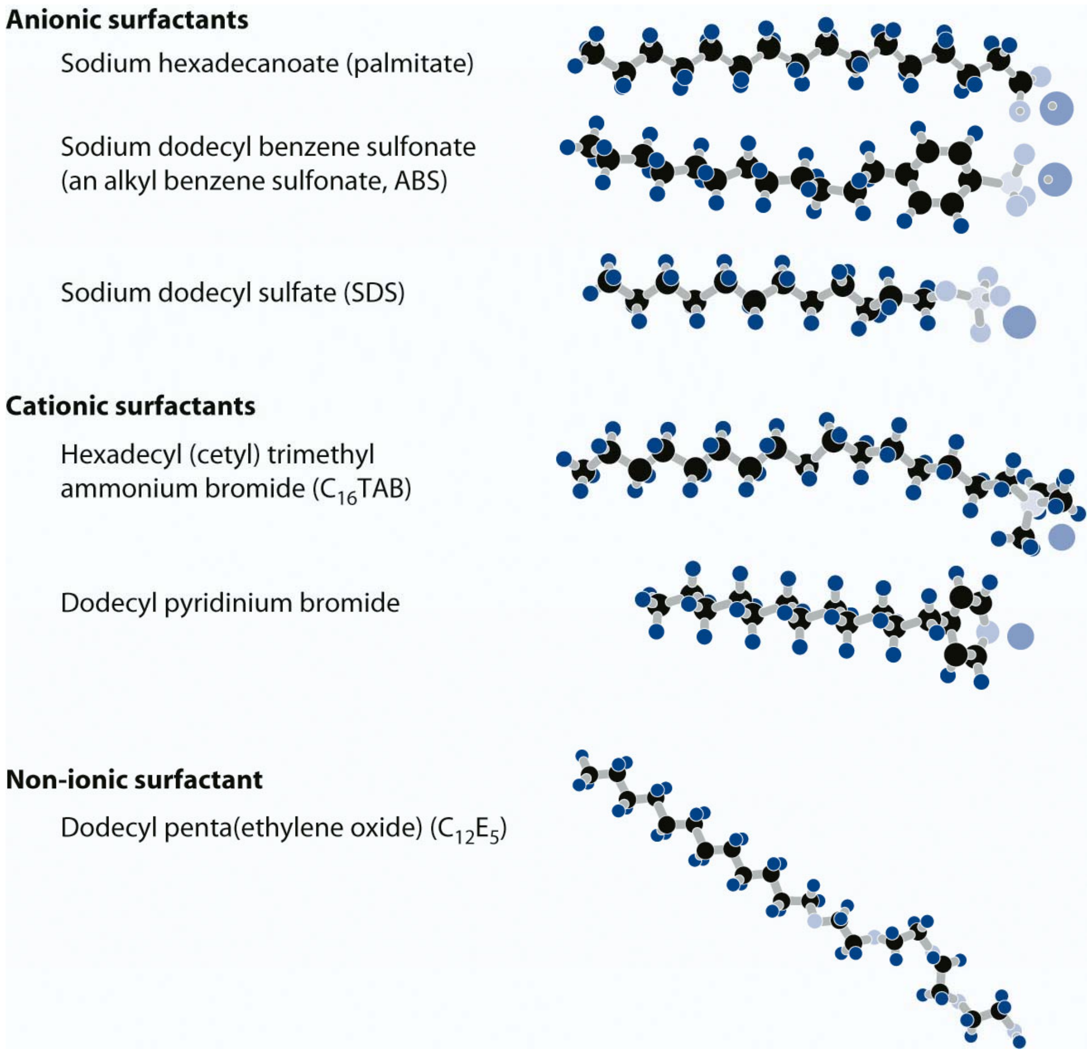


- **Gibbs monolayers**



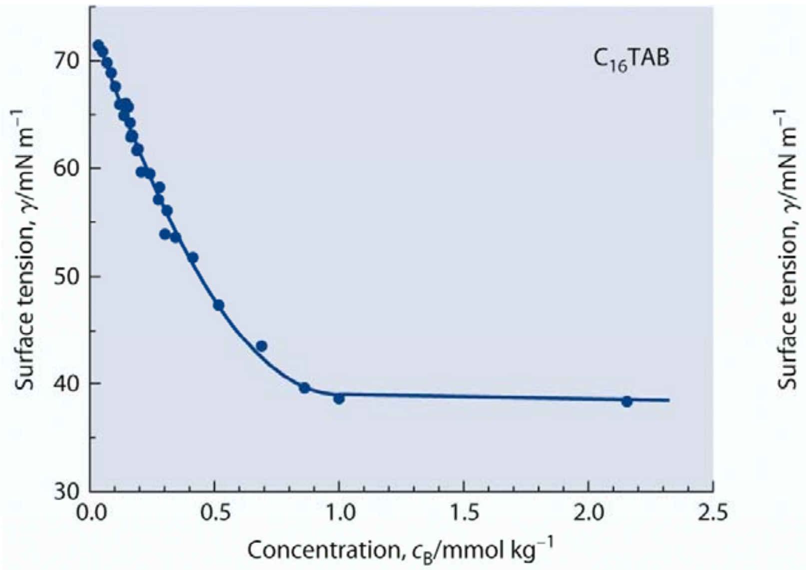
Absorption of surfactants

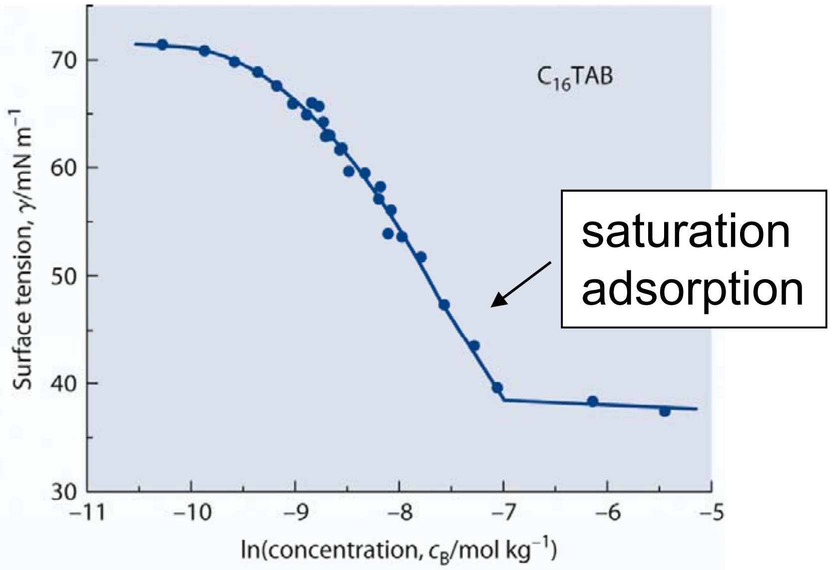
- Surfactants can be:
  - anionic,
  - cationic,
  - non-ionic

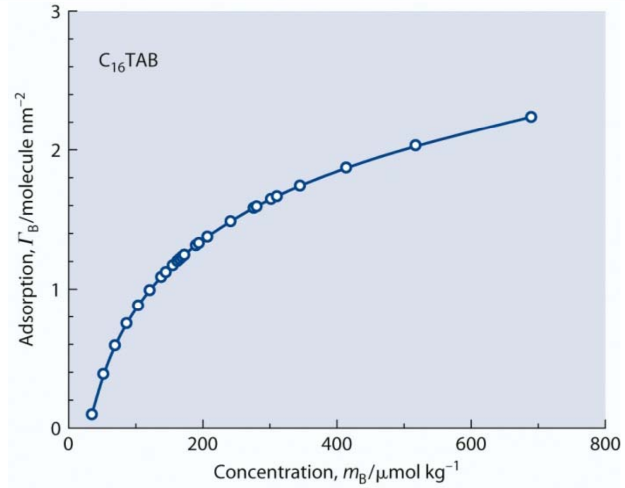


Absorption of surfactants

- Surface tension of surfactant usually falls to a lower limit and becomes a constant after







Absorption of surfactants

- Gibbs equation occasionaly reveals discrepancies with experimentally measured values.
  - surface hydrolysis: one of the ions is not adsorbed by the surface and replaced by H^+.

$$-\frac{d\gamma}{RT} = \Gamma_{M^+} d\ln(c_{M^+}) + \Gamma_{X^-} d\ln(c_{X^-}) + \Gamma_{H^+} d\ln(c_{H^+})$$

Γ_{M^+} =0; c_{H^+} =const

$$-\frac{d\gamma}{RT} = \Gamma_{X^-} d\ln(c_{X^-})$$

  - indifferent electrolyte: same situation can be created artificially to avoid ambiguities that might arise due to surface hydrolysis by adding large amounts of M^+Y^-:

$$-\frac{d\gamma}{RT} = \Gamma_{M^+} d\ln(c_{M^+}) + \Gamma_{X^-} d\ln(c_{X^-}) + \Gamma_{Y^-} d\ln(c_{Y^-}) \Rightarrow -\frac{d\gamma}{RT} = \Gamma_{X^-} d\ln(c_{X^-})$$

c_{M^+} =const; Γ_{Y^-} =0

Micelles

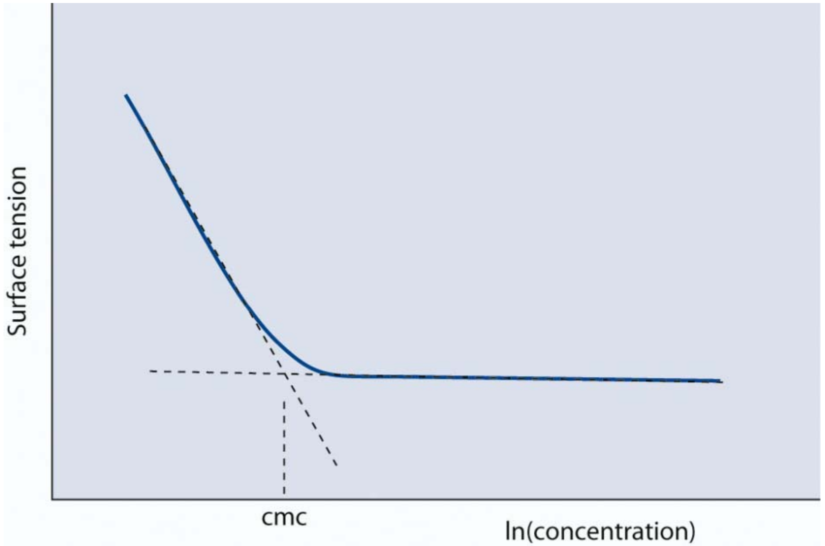
- above certain critical concentration the surface tension becomes independent of concentration: **critical micelle concentration (cmc).**

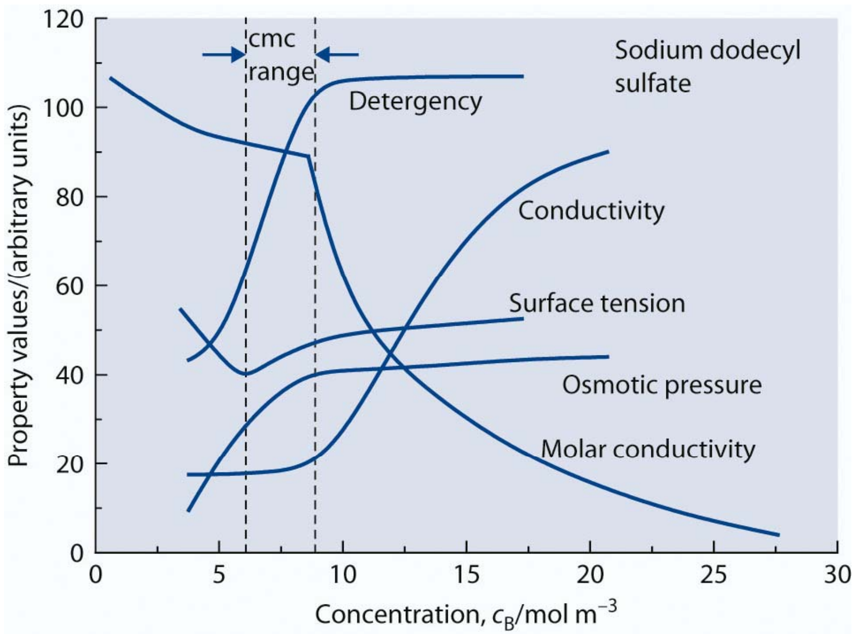
$$-\frac{d\gamma}{RT} = \Gamma_{X_S}\, d\ln(c_{X_S}) + \Gamma_{X_M}\, d\ln(c_{X_M})$$

not all amphiphiles form micelles.

- at **cmc** other properties show distinct changes as well (e.g. osmotic pressure indicate that the number of “solute particles” stays the same above cmc).

- formation of micelles means decrease in G, primarily due to large **increase** in entropy: hydrophobic interaction.





Probelms

- **Problems 1, 2, 3**