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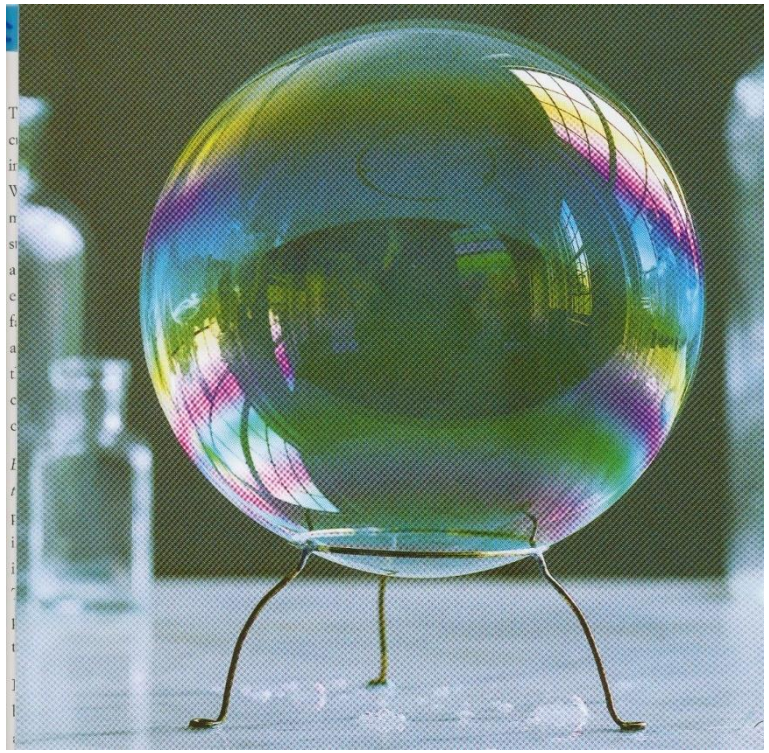
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Gibbs Adsorption Isotherm

Lecture 35

Adsorption onto Solids



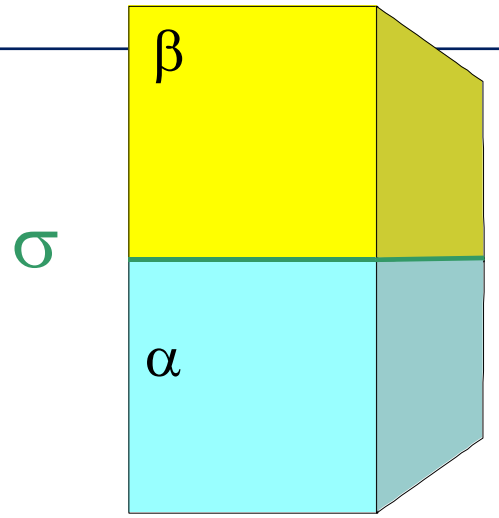
Lecture 37

MOFs

Surfaces of liquids

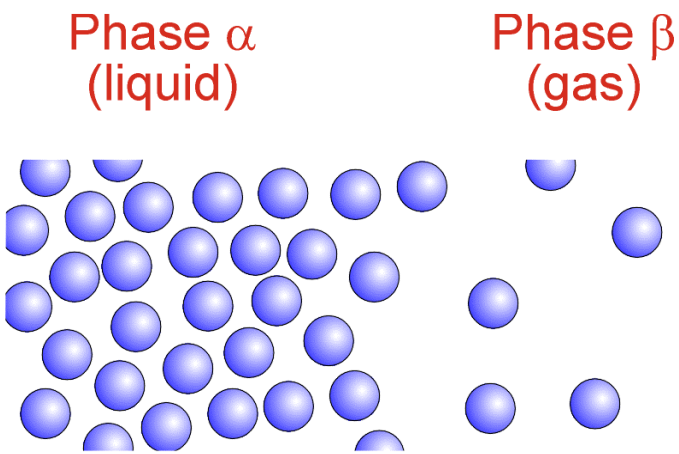
Consider a system composed of two macroscopic fluid phases, α and β, each consisting of one component (e.g. water/steam)

Phases α and β are separated by an interface σ.



On an atomistic scale, however, the interface is ill-defined due to fluctuations

- Where exactly is the interface?
- How do you measure the amount of something adsorbed on a dynamic, deformable interface?



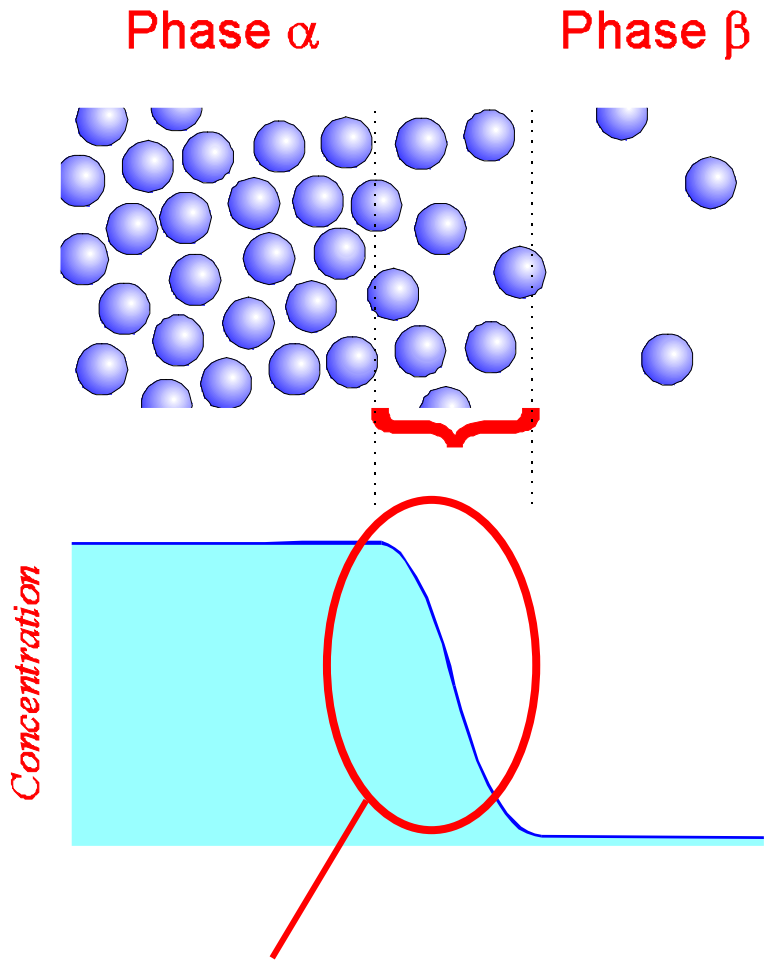
The interface is a region

An instantaneous snapshot of the system shows a change in concentration from its bulk α value to its bulk β value.

This means that the interface is actually a region of changing composition.

By averaging over time, we can characterise the "interphase" region in terms of its width and the rate of change of composition within it.

A graph of concentration versus position, passing through the "interphase" region, would look like this:



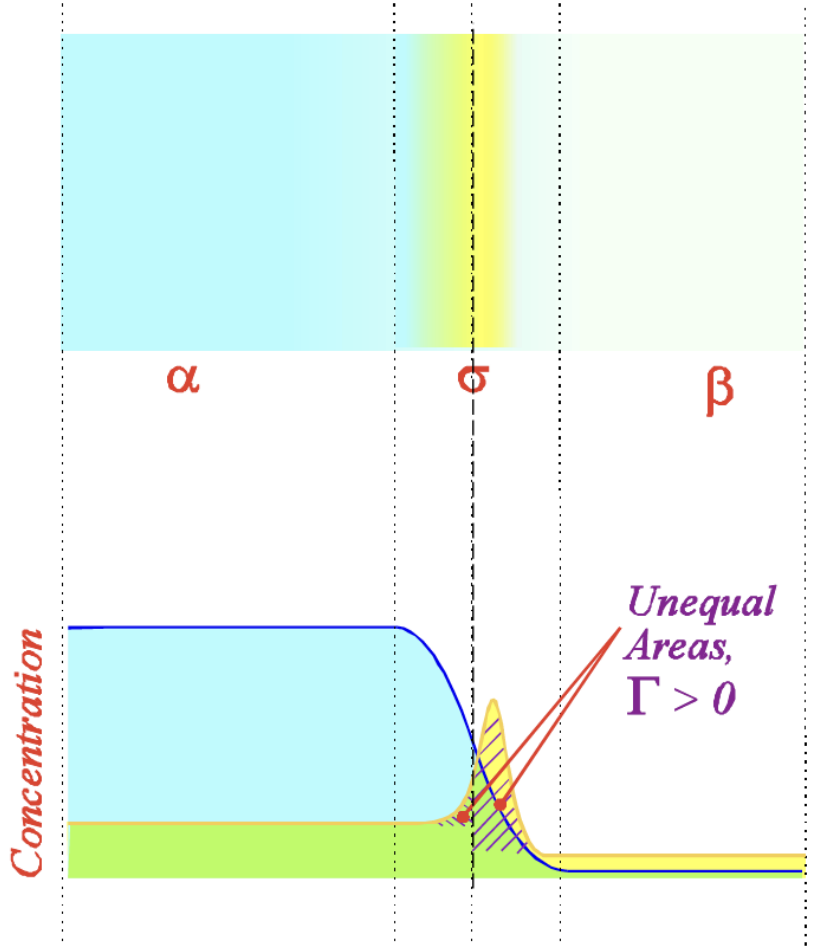
Adsorption of a second component

Q1

Now we add a second component represented by the yellow shading.

This component is:

- more soluble in phase α,
- less soluble in phase β, and
- adsorbed at the interface between α and β.



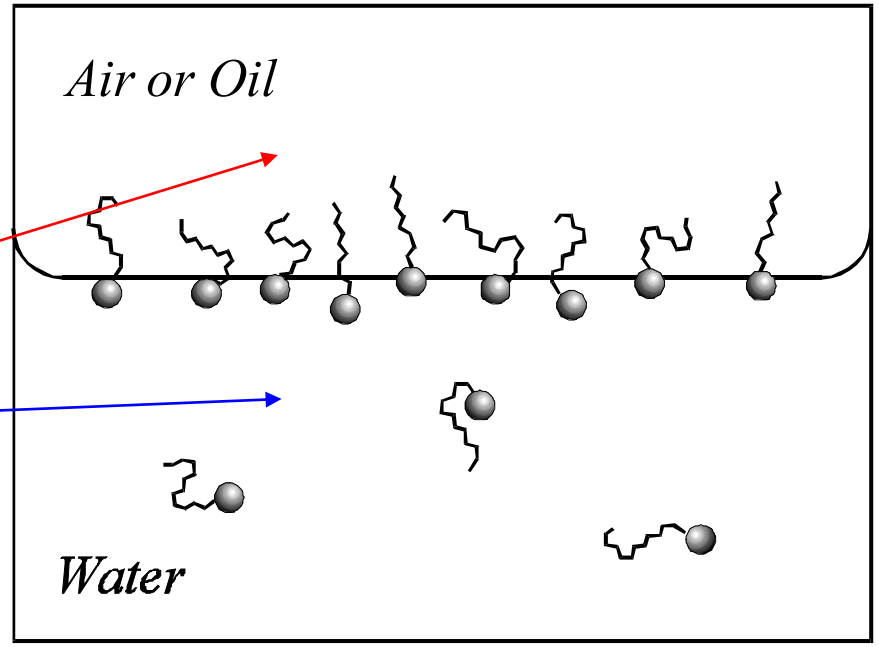
Molecular picture of adsorbed layer structure

At the surface of water, the dielectric constant ε drops from 78 to about 1 (ε of air).
At a water/oil interface, ε drops from 78 to about…

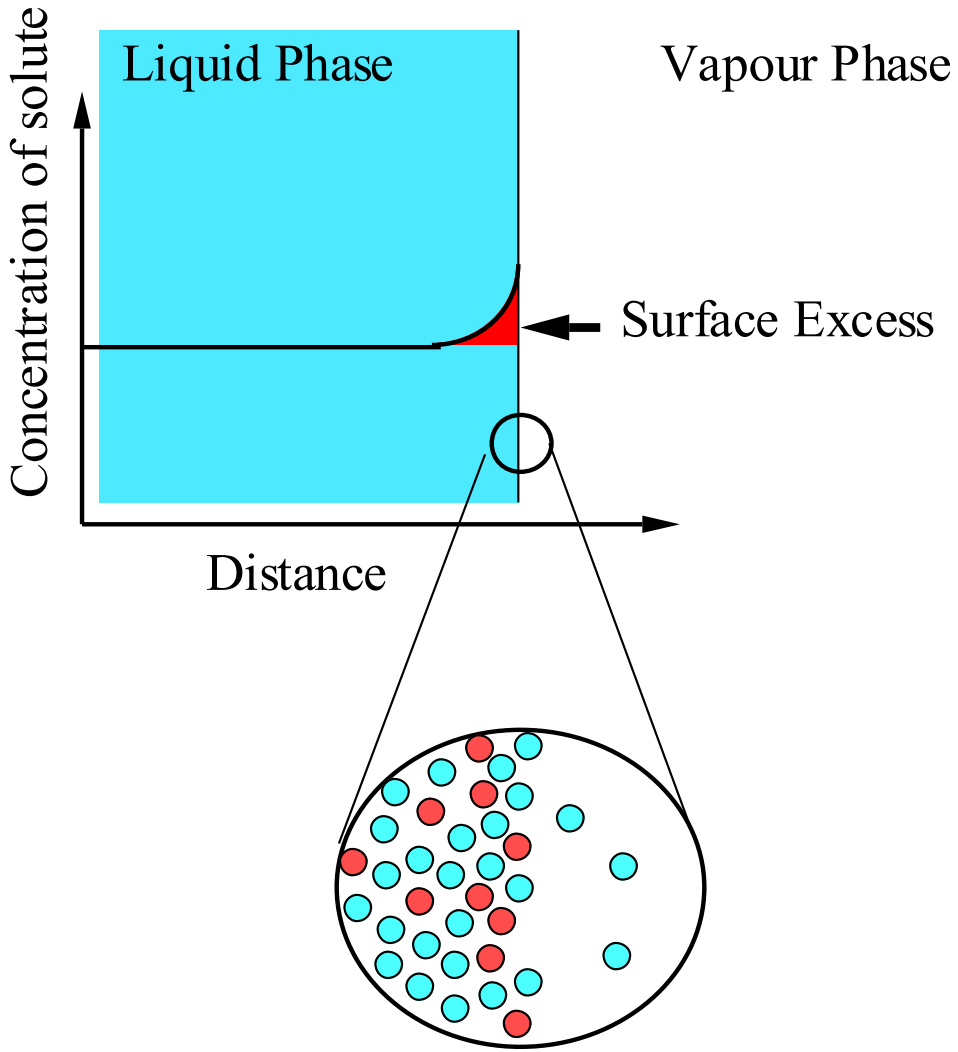
1.89 for n-hexane 1.99 for n-decane 2.38 for toluene

i.e. Polar → Non-polar

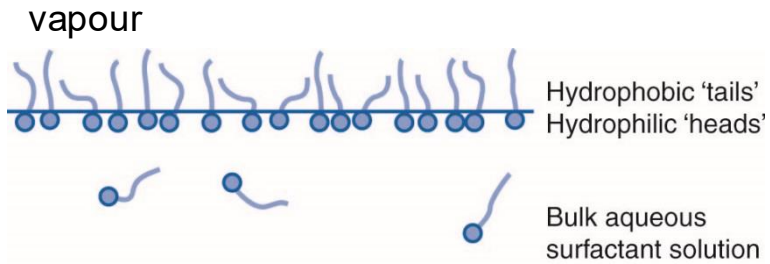
Amphiphilic Molecules orient themselves with their non-polar 'tails' in the non-polar medium (air or oil) and their polar 'heads' in the polar medium (water).



Surface excess



E.g. a surfactant



If a solute increases in concentration near the surface, it is said to be "surface active" and we say that there is a **surface excess:**

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

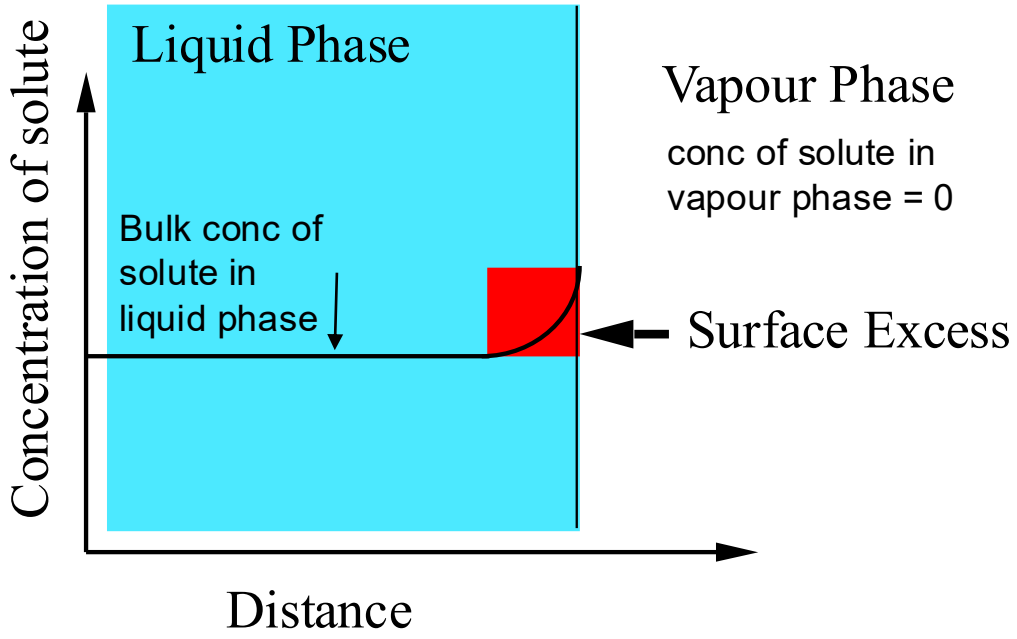
n_i = number of extra moles of i at the interface
A = surface area of the interface

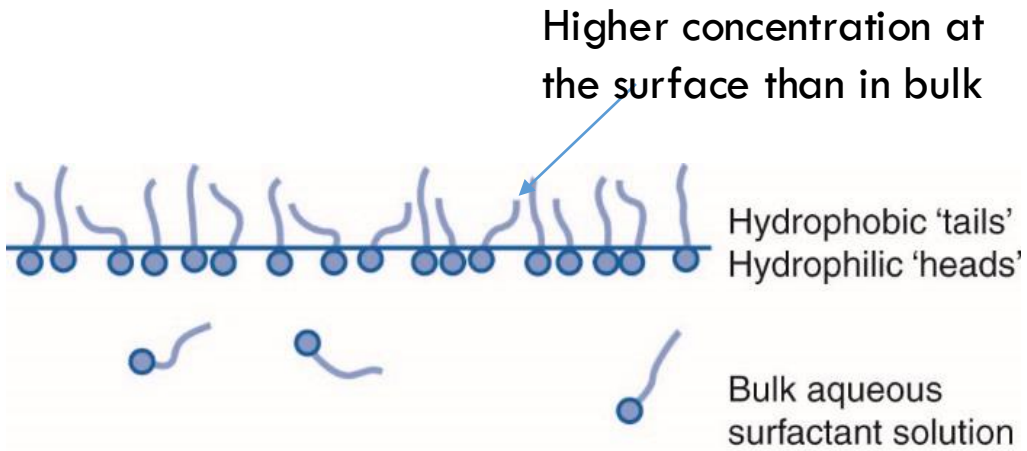
Clearly, Γ has units of mol / m^2

Surface excess continued

Q2

- The *surface excess* of any component in the interface may be positive, negative, or zero.
- Positive Γ means that the component accumates at the interface (surfactants do this)
- Negative Γ means that the component is depleted at the interface (surfactants don't do this)
- Should we expect a relationship between the surface excess (Γ) and the surface tension (γ) ?





The Gibbs Adsorption Isotherm

The Gibbs Isotherm provides that relationship!

For an ideal solution it is:

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

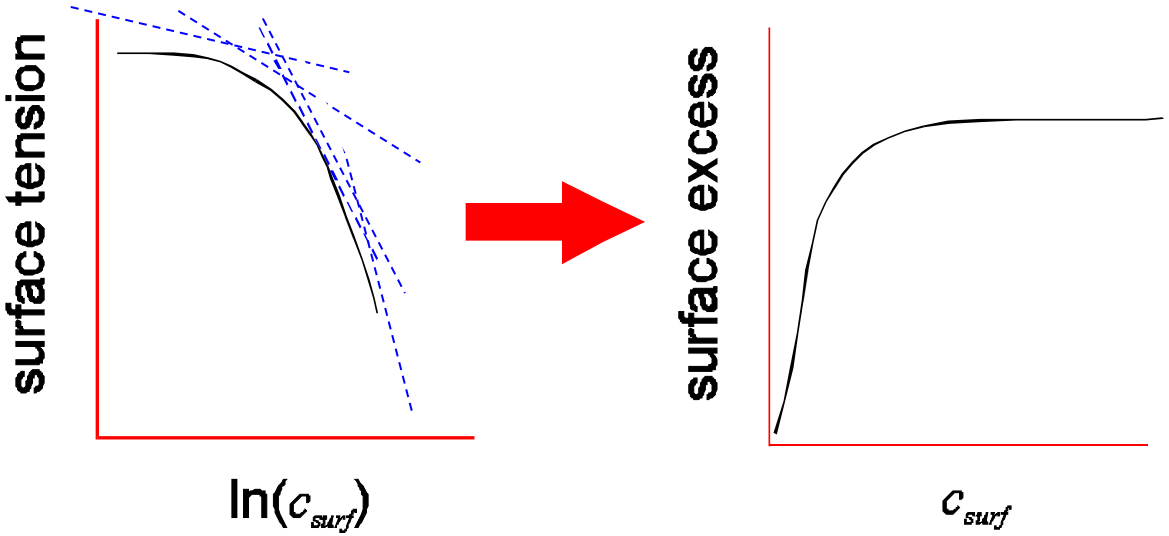
True for a single adsorbing species
e.g. non-ionic surfactant

"The slope of surface tension versus ln c_i is proportional to the surface excess of component *i*"

The proportionality constant is negative, so:

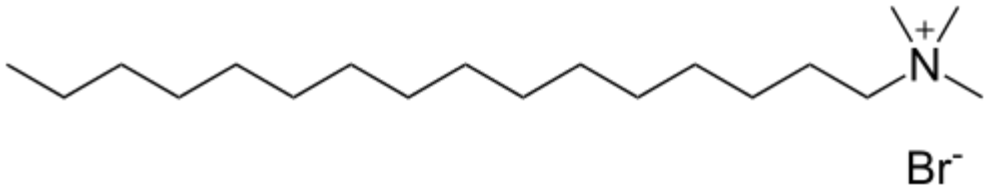
A positive surface excess Γ decreases γ.

A negative surface excess Γ increases γ.



Gibbs adsorption isotherm for charged surfactants

For salts or ionic surfactants, such as CTAB, two species (CTA^+ and Br^-) adsorb at the interface.

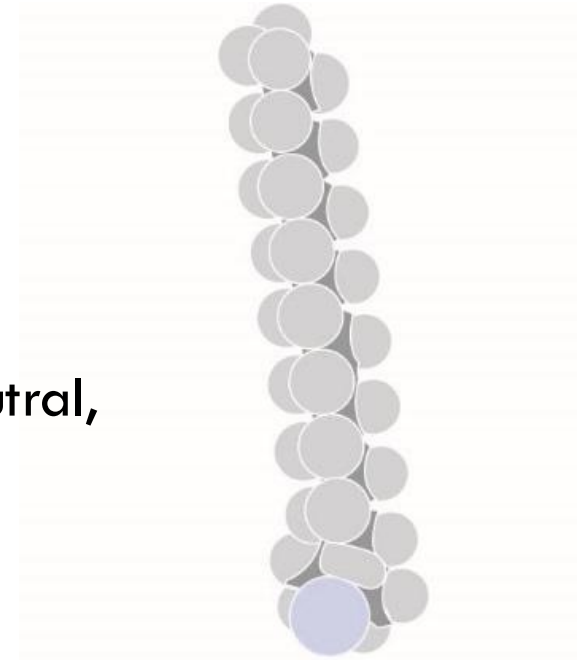


In this case the equation becomes

$$\Gamma_i = \frac{-c_i^+}{2RT}\,\frac{d\gamma}{dc_i^+}$$

because the bulk chemical potentials of both ions change (equally) with concentration of the surfactant. The interface must remain electrically neutral, i.e.

$$\Gamma_{Na^+} = \Gamma_{Cl^-}$$



Cetyl trimethyl ammonium bromide

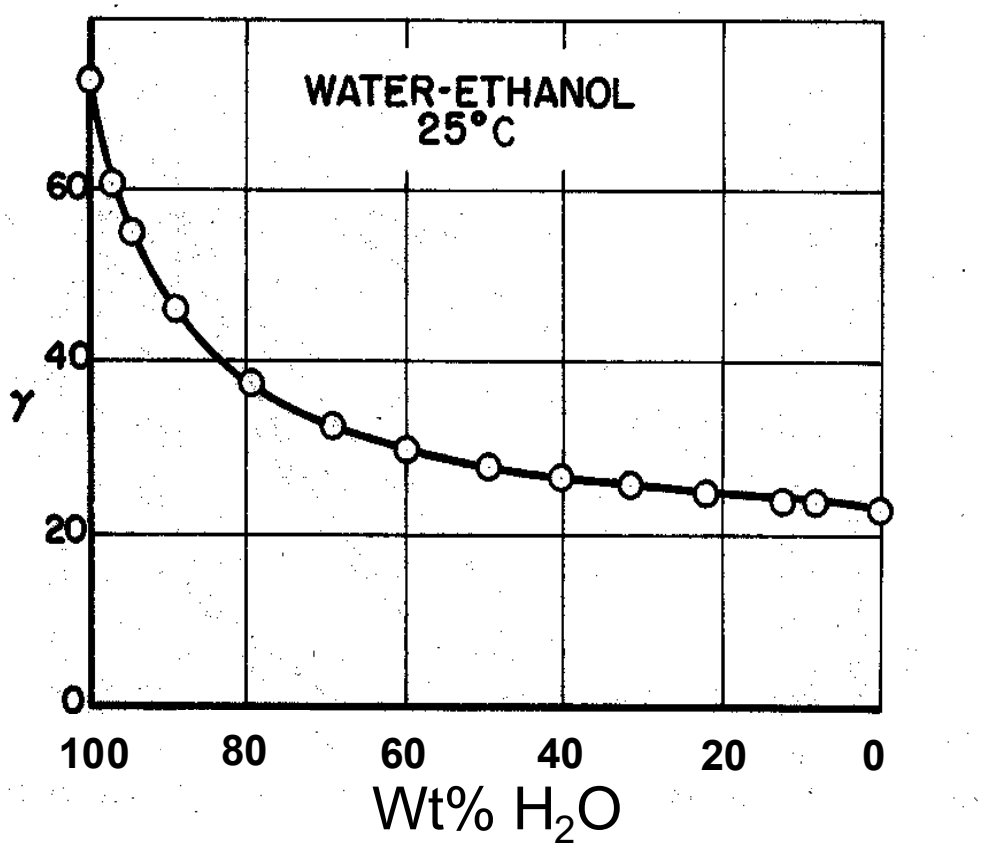
Surface tension of ethanol/water mixtures

Imagine slowly adding ethanol to water.

As the concentration of ethanol increases, γ decreases.

=> a positive surface excess for dissolved ethanol. That is, ethanol molecules accumulate at the air-water interface.

In contrast, if we slowly add water to ethanol, γ increases, indicating that water is excluded from the ethanol/air interface.



Surface tension of NaCl(aq) solutions

Q3

As the concentration of NaCl is increased, γ increases.

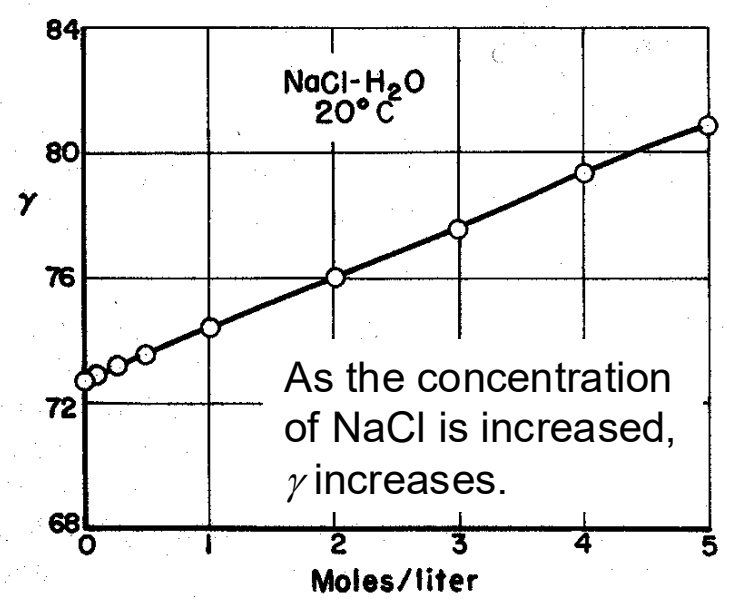
$\Rightarrow$ a <u>negative</u> surface excess for dissolved NaCl.

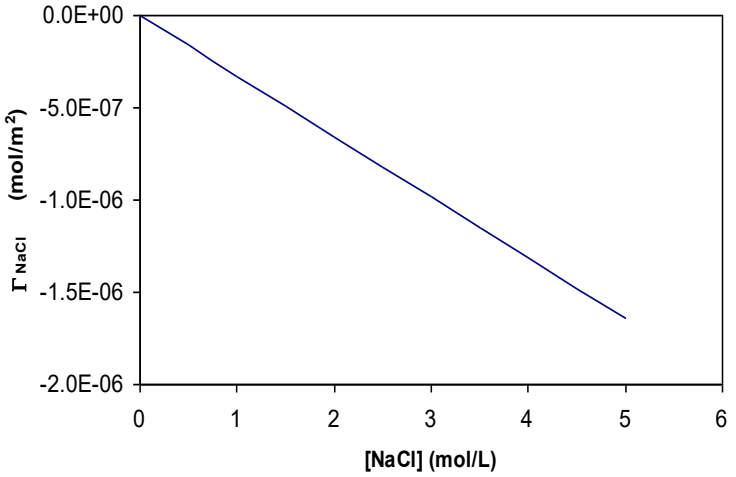
That is, Na^+ and Cl^- ions do not accumulate at the air-water interface.

They are depleted from the interface and remain in the bulk solution.

Structure of ionic solution interfaces is still an active area of research!

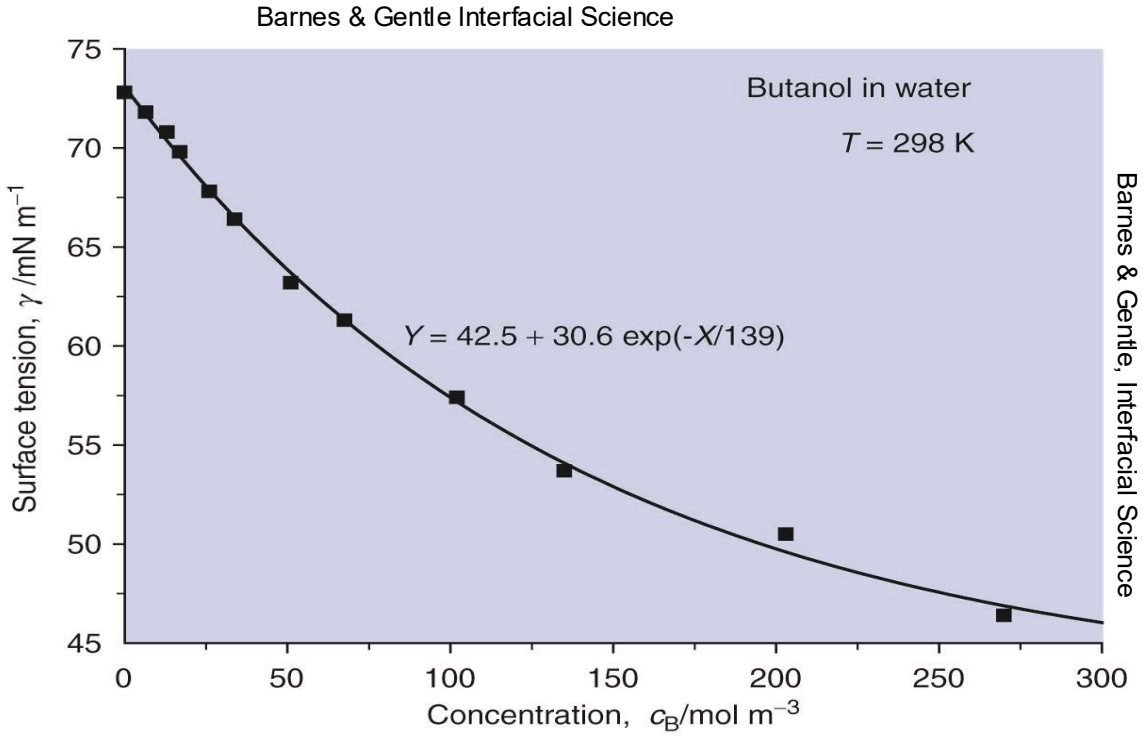
https://www.nature.com/articles/s41557-023-01416-6





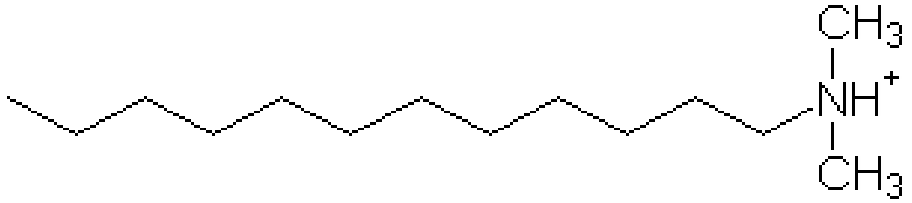
Exercise (see week 13 tutorial)

- The surface tension of a water solution of butanol was measured at 298 K and gave the following graph.

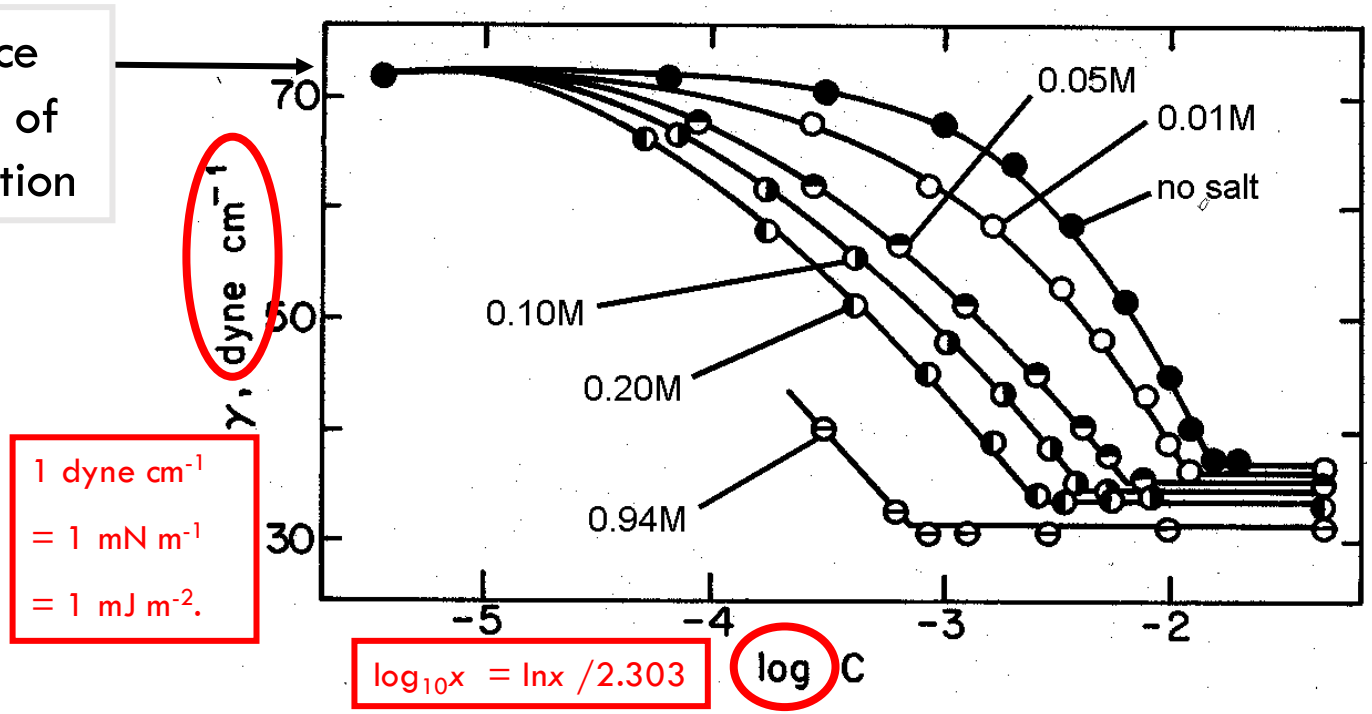


Effect of salt on dilute surfactant solutions

dodecyldimethylammonium (DDA+) chloride in water with NaCl

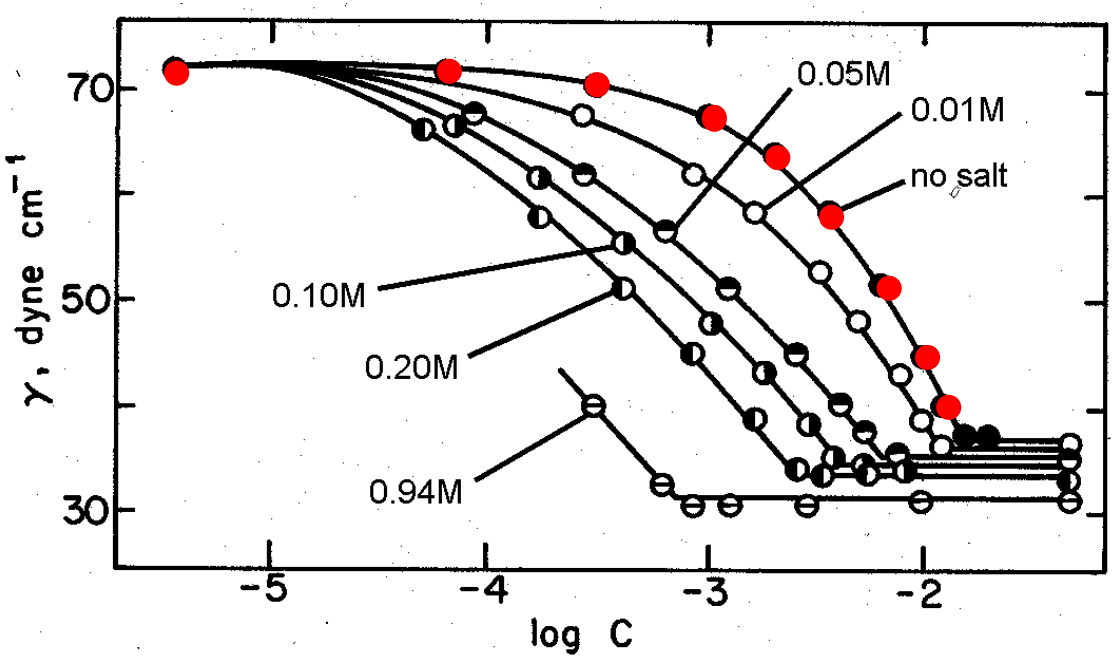


Surface tension measurements of a DDA+ solution, with various amounts of salt

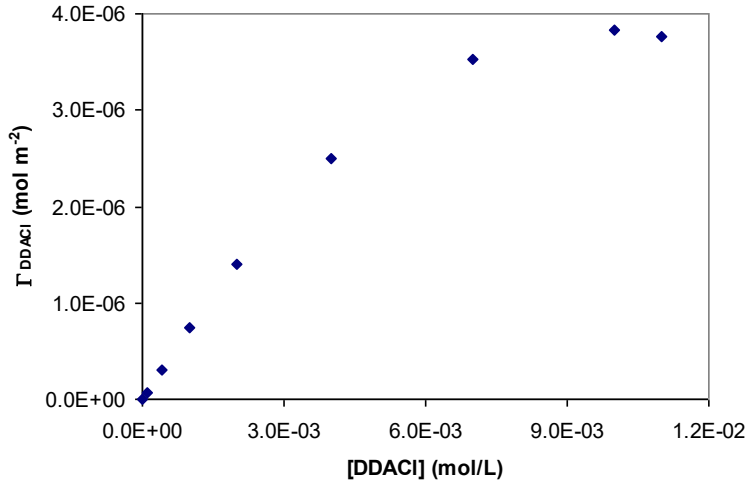


Dilute surfactant solution – no salt added

$$\Gamma_{DDA+} = \frac{-1}{2RT} \frac{d\gamma}{d\ln[DDA^+]}$$



Surface tension decreases with increasing concentration, so the surfactant has a **positive** surface excess.



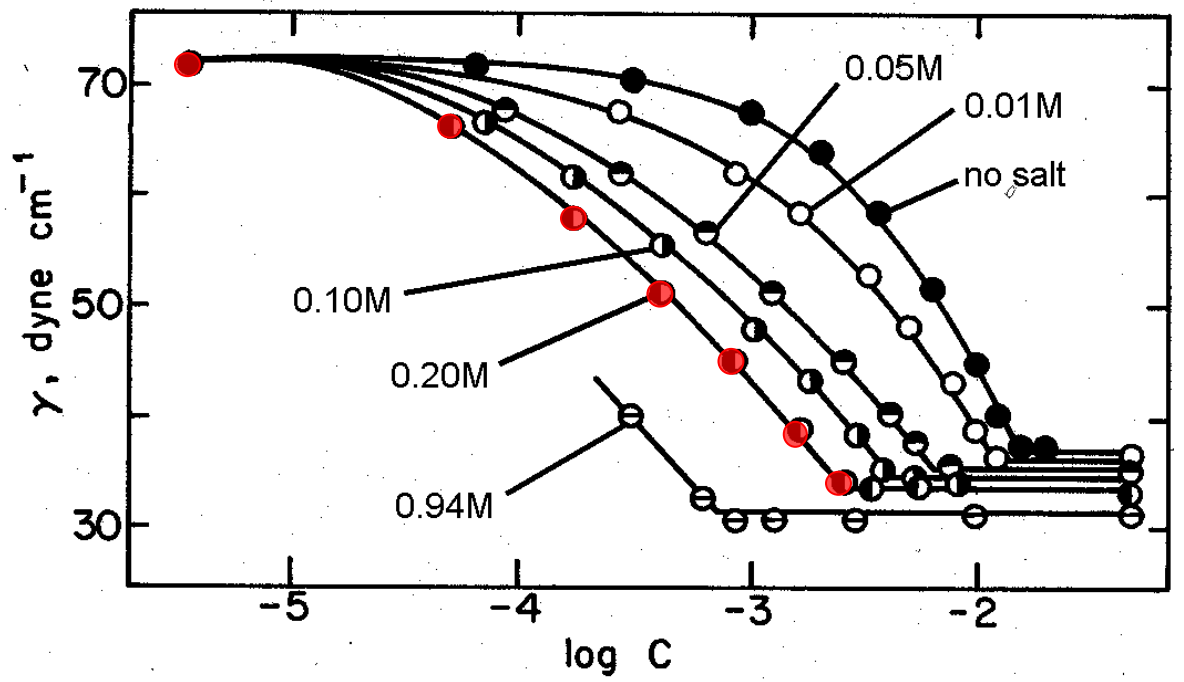
Dilute surfactant solution – lots of salt added

Now we consider [NaCl] = 0.20 M. The Gibbs isotherm includes both NaCl and DDACl.

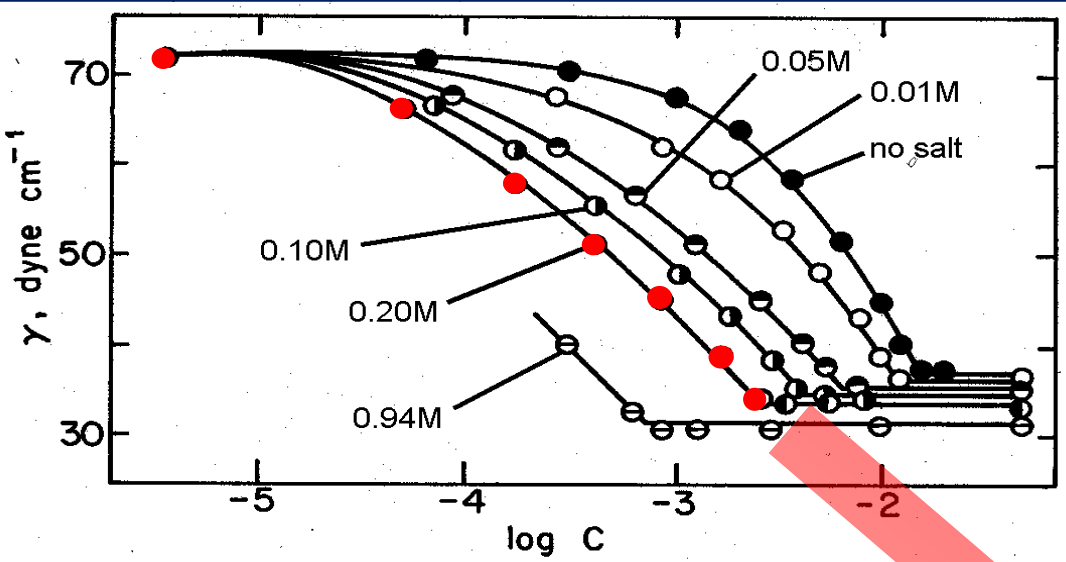
$$-d\gamma = \Gamma_{DDA^+} RTd\ln[DDA^+] + \Gamma_{Na^+} RTd\ln[Na^+] + \Gamma_{Cl^-} RTd\ln[Cl^-]$$

When the concentration of added Na^+ and Cl^- is much larger, only the concentration of the DDA^+ ion is effectively changing.

Hence $$\Gamma_{DDA^+} = \frac{-1}{RT}\frac{d\gamma}{d\ln[DDA^+]}$$



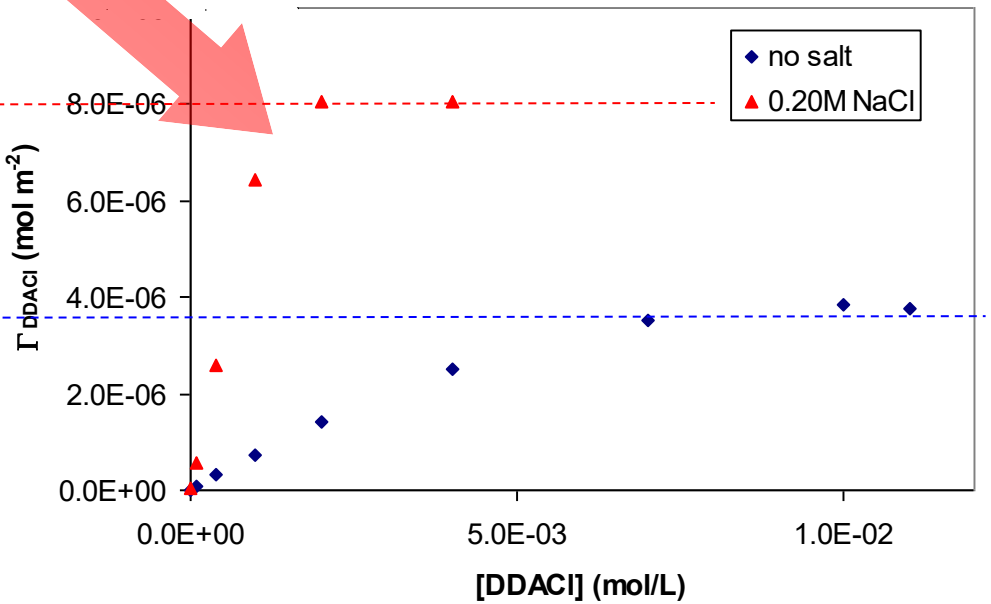
Using the Gibbs adsorption isotherm



Why is surface excess of the surfactant higher when NaCl is added?

Γ_{max} = 8.1 x 10^{-6} mol m^{-2}

Γ_{max} = 3.8 x 10^{-6} mol m^{-2}



Area/molecule in an adsorbed monolayer

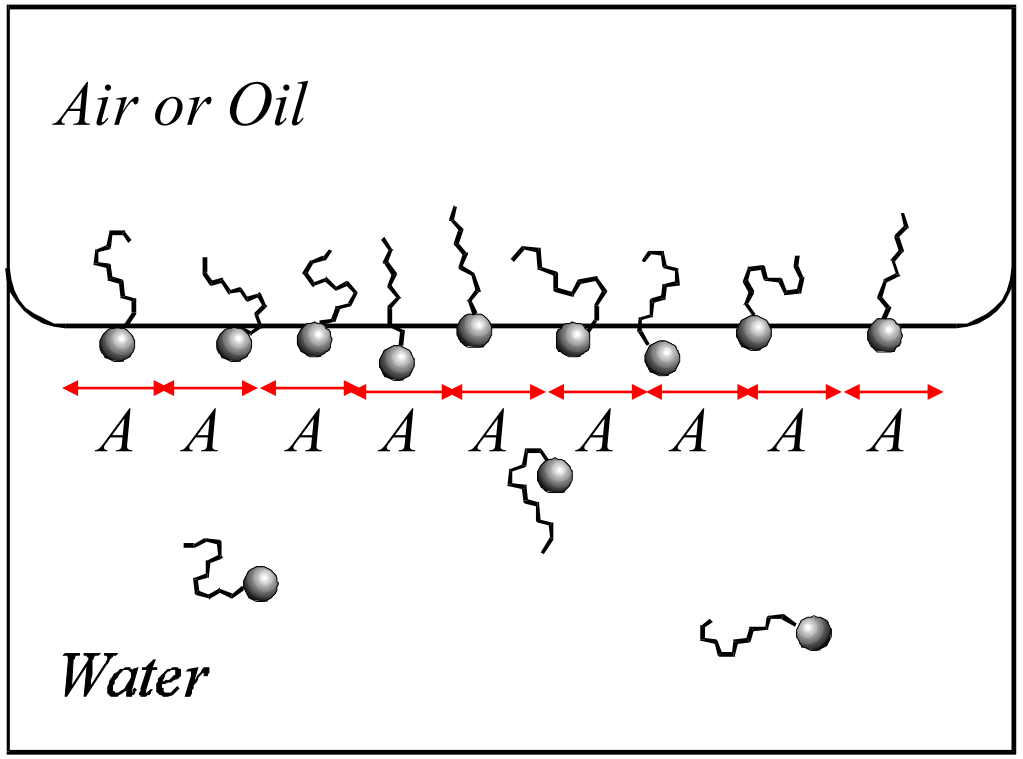
A monolayer is formed at the interface. This monolayer (and therefore the interface) is about 20 Å thick.

If the adsorbed layer is actually a monolayer, then the surface excess can be used to calculate the average area occupied by a molecule at the interface.

$$A = \frac{1}{N_A \Gamma}$$

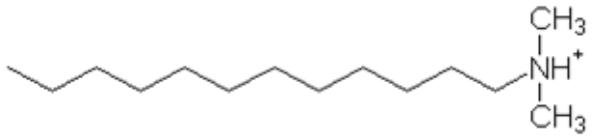
$\mathrm{m}^2/\mathrm{molecule}$

Surface excess of the surfactant ion only.



Size of the head group

For ionic amphiphiles like dodecyldimethylammonium



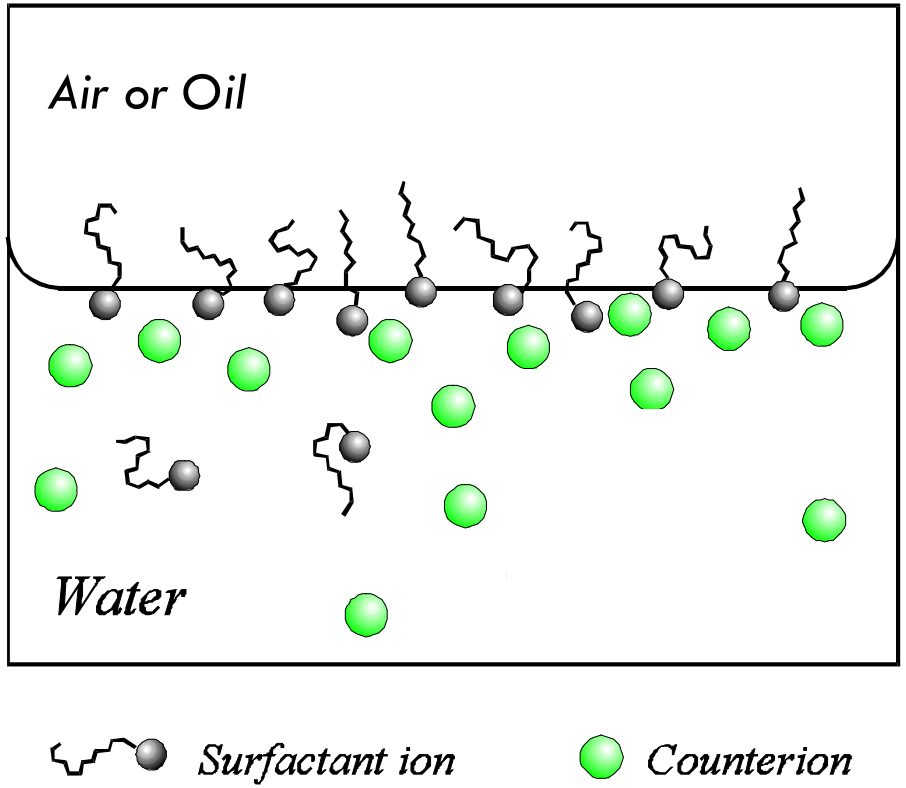
or dodecylsulfate



A monolayer is formed by the surfactant at the interface and the counterions are attracted to that adsorbed layer.

For a monolayer of DDA^+ in pure water, A = 45Å^2/molecule.

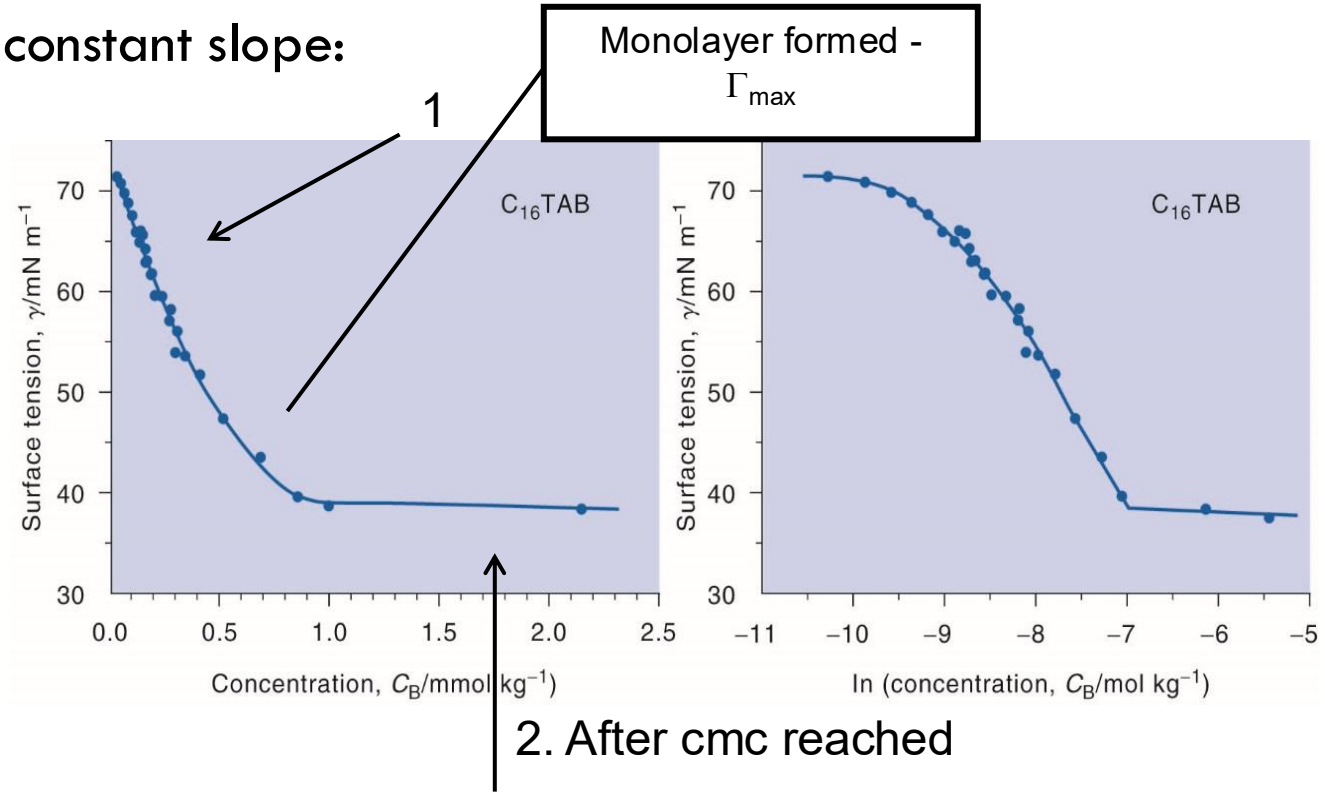
In 0.2M NaCl, A = 20Å^2, because the electrostatic repulsion between molecules is screened



Critical micellar concentration (cmc)

Surfactant adsorbs at the air/water interface, until it forms a monolayer.
Then the surface tension exhibits a break at a particular concentration, the critical micelle concentration or *cmc*.
Above this concentration the surface tension remains constant as concentration of surfactant is increased.
There are two regions of almost constant slope:

1. When the monolayer forms
2. Beyond the cmc



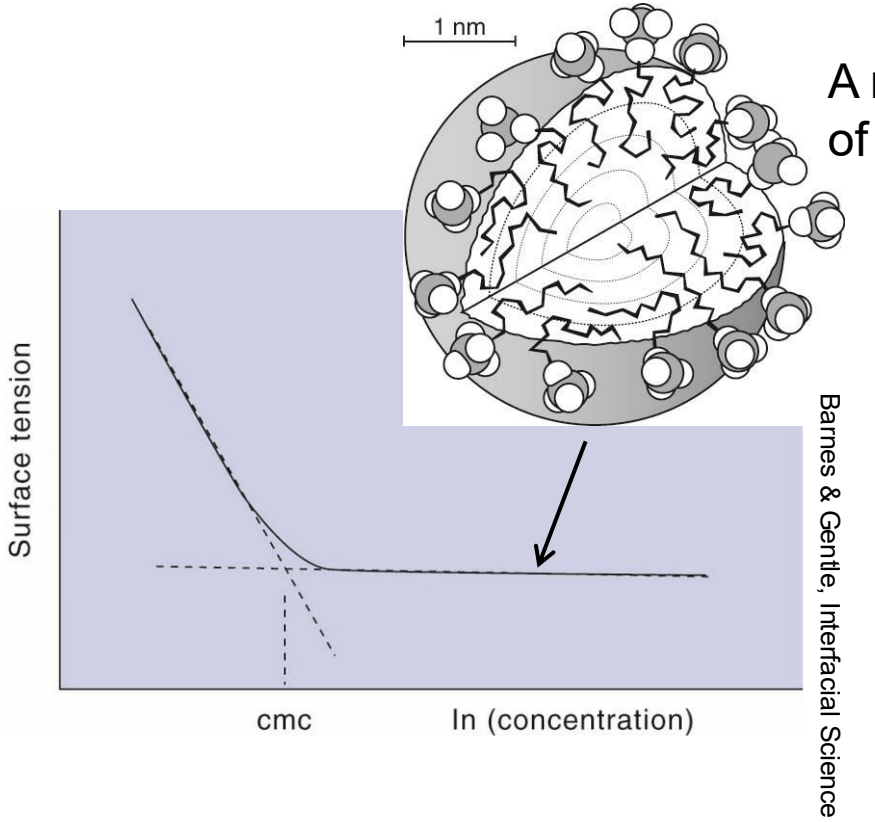
Barnes & Gentle, Interfacial Science

Why is surface tension constant above the cmc?

Once the cmc is exceeded and micelles are present in solution, the monomer concentration is fixed. That is, like a solubility equilibrium, adding more surfactant makes more micelles *without increasing the concentration of dissolved monomeric surfactant.*

Micelles are not surface active ($\Gamma = 0$), so fixing the monomer concentration fixes surface tension hence $d\gamma = 0$.

As a results, the surface tension is constant above the cmc.



Learning outcomes

After this lecture you should be able to

- Explain surface excess (positive and negative).
- Explain the relationship between surface tension and adsorption.
- Use the Gibbs isotherm to relate surface excess to surface tension.
- Specifically, understand and apply the Gibbs isotherm to a range of ionic solutes.
- Calculate molecular area from surface excess for monolayer adsorption, and *vice versa*.
- Describe the effect of added salt on surfactant monolayer density.
- Recognise the characteristics of micelle formation in a surface tension curve.