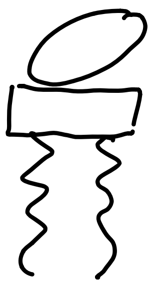
Biological Membranes

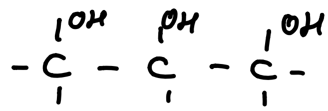
26. Oct. 2019

Lipid chemistry:

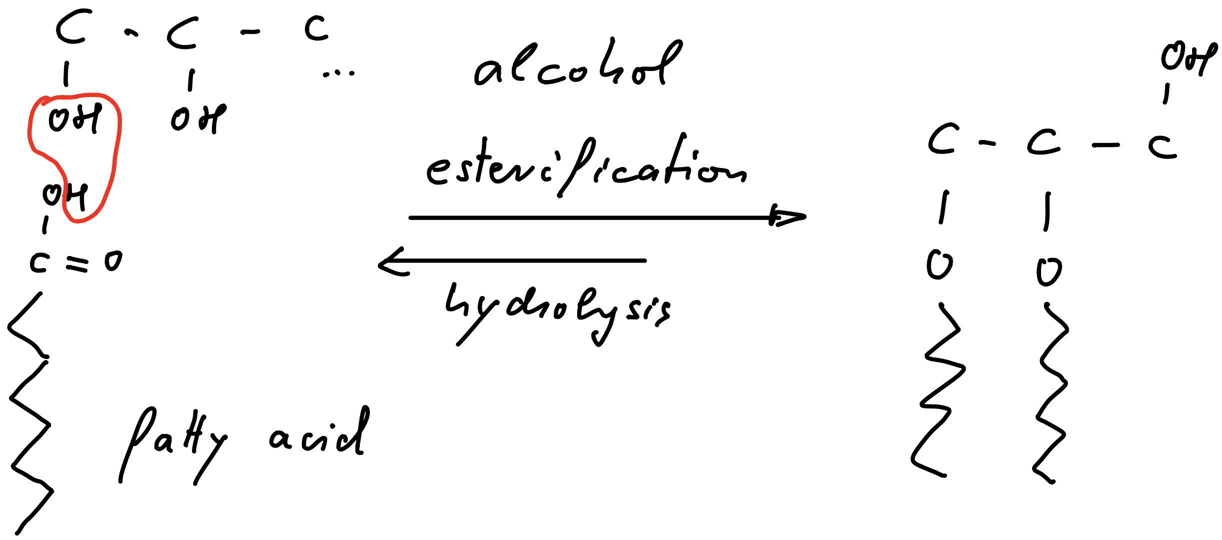


headgroup e.g. choline

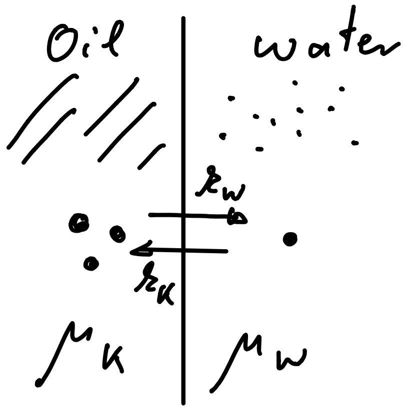
backbone glycerol



tails alkyl chains $\sim \hat{=} CH_3-CH_2-CH_3 \cdots$



Solubility of hydrocarbon chains in water



$$\mu_i = \mu_i^0 + kT \ln X_i$$

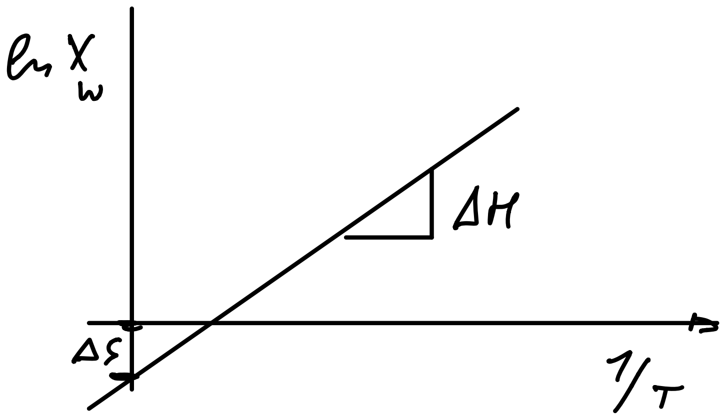
in thermodyn. Eq. $\mu_W = \mu_K$

if $X_K \approx 1$ (hydrophobic molecule)

$$\boxed{\ln X_W = (\mu_K^0 - \mu_W^0)/kT}$$

Measure X_W (e.g. opt. absorption spectrosc.)

$$\Rightarrow \mu_W - \mu_K = H^{\bullet}_W - H^{\bullet}_K - T(S_W - S_K)$$



	$\Delta\mu$	ΔH	ΔS
C_2H_4	16,3	-10,5	-8,8
C_3H_6	20,3	-7,1	-9,2
C_6H_8	24,7	-3,3	-9,6

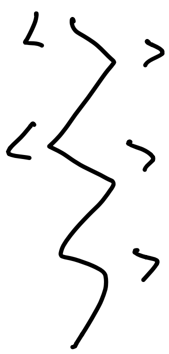
in kJ/Mol

$$\boxed{\Delta\mu \approx -10{,}2 + 3{,}7 \cdot n_{CH_2}}$$

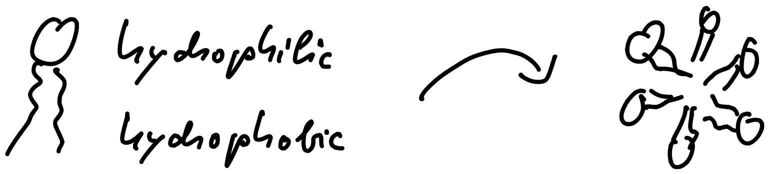
1.) Transition reaction k_W is exotherm !

2.) Entropy of molecule decreases in water

⇒ Ice berg effect



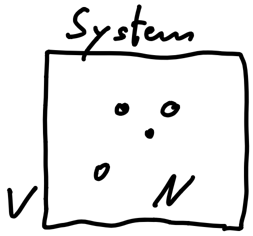
water forms structure at hydrocarbon surface



"Micelle"

what drives it?

Thermodynamics of self-assembly:



U: inner energy

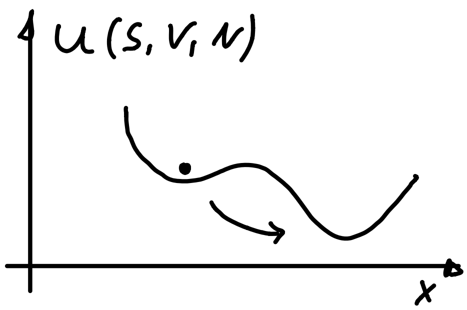
$S = k \cdot \log \Omega$ entropy

Ω: multiplicity

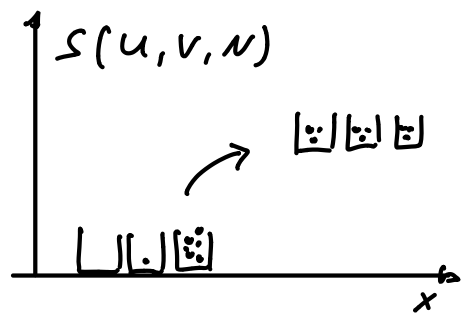
N: number of particles

V: volume

Minimum energy



Maximum entropy



Helmholtz free energy : $F = U - TS$

Extremum principle : system moves to lowest F

Equilibrium : $\frac{dF}{dx} = 0$ and $\frac{d^2F}{dx^2} > 0$

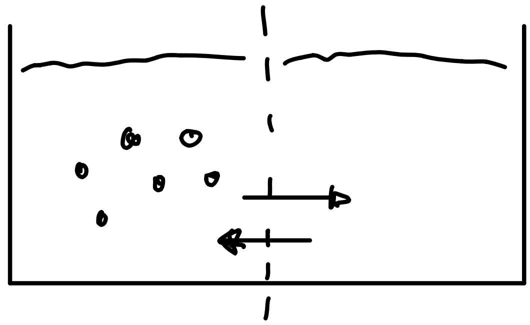
In test tube experiments :

constant (T, p, N) → use Gibbs free energy $G = G(T, p, N)$

$$\boxed{G = H - TS}$$

, $H = U + pV$ enthalpy

Open system : solutions



$$x_i = \frac{n_i}{\sum n_i} \quad \text{mol fraction}$$

$$c_i = \frac{n_i}{V} \quad \text{molarity}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial N}\right)_{T,p} dN$$

$$= -S\,dT + V\,dp + \sum_i \mu_i\,dN_i$$

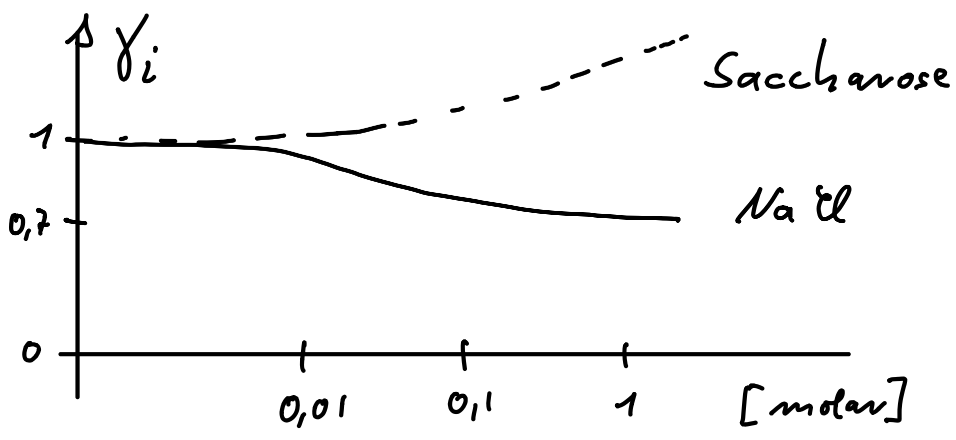
$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$ chemical potential of species i

$\hat{=}$ free energy per molecule

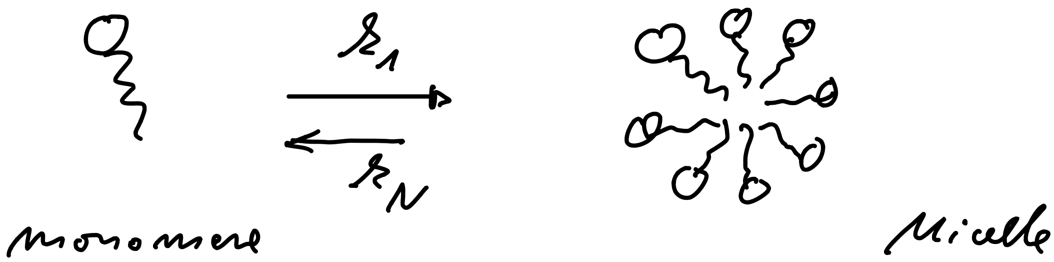
In ideal solutions: $\boxed{\mu_i = \mu_i^0 + kT \log x_i}$

In real solutions: $\mu_i = \mu_i^0 + kT \log a_i$

with activity $a_i = \gamma_i x_i$ and γ_i : activity coefficient



Thermodynamics of lipid aggregation



X_1 : molar fraction monomers

X_N : molar fraction of lipids in micells

$\tilde{X}_M = \frac{X_N}{N}$: molar fraction of micelles

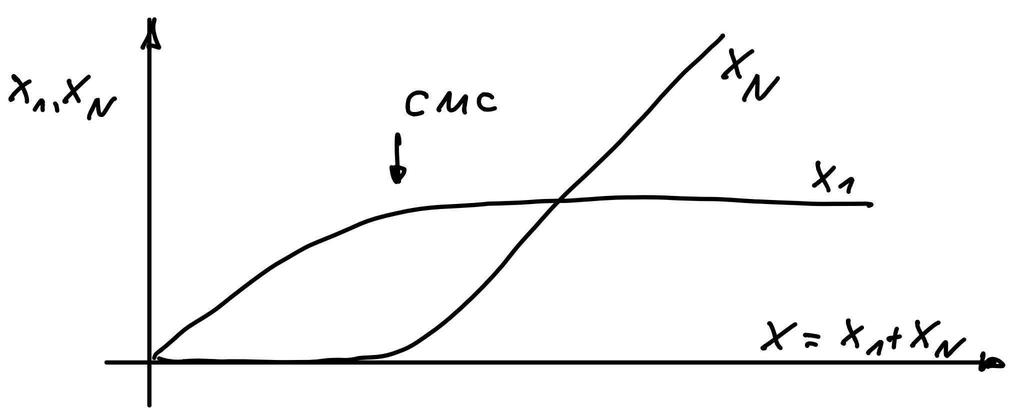
$$\mu_1 = \mu_1^0 + kT \log X_1$$

$$\mu_{micelle} = N \cdot \mu_N^0 + kT \log \frac{X_N}{N}$$

$$\mu_N = \mu_N^0 + \frac{kT}{N} \log \frac{X_N}{N}$$

with $\mu_1 = \mu_N$ follows:

$$X_N = N \left[X_1 \exp\left[\frac{\mu_1^0 - \mu_N^0}{kT} \right] \right]^N$$



Def. Critical micelle concentration

CMC : if $X_1 = X_N$ (half the lipids are in micelles)

if $X_N > X_1$ then $X_1 \geq X_{1,\text{crit.}} = CMC$

$$CMC = \exp\left[\frac{-(\mu_1^\circ - \mu_N^\circ)}{kT}\right] = e^{-\alpha}$$

$$\Delta\mu = (11.3 - 3\, n_{CH_2})\ kJ/mol$$