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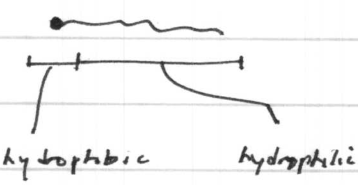
NM - self-assembly in solution

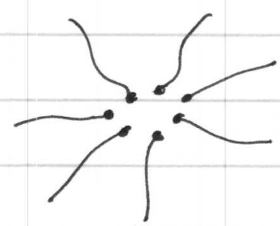
→ formation of aggregates ("micelles")

consider amphiphilic molecules (greek root = "both + friendship")

e.g.,



⇒ will aggregate in solution like



(in H_2O, hydrophobic ends → inward)

so let's consider a solution of amphiphiles, or generally any monomer

(monomer = one part in assembly of many parts)

define X_N = dimensionless molar fraction of components (monomers) in solution as the N^{th} aggregate, so the concentration of the N^{th} aggregate is

$$C_N = \frac{X_N}{N}$$

total molar fraction of monomers in solution:

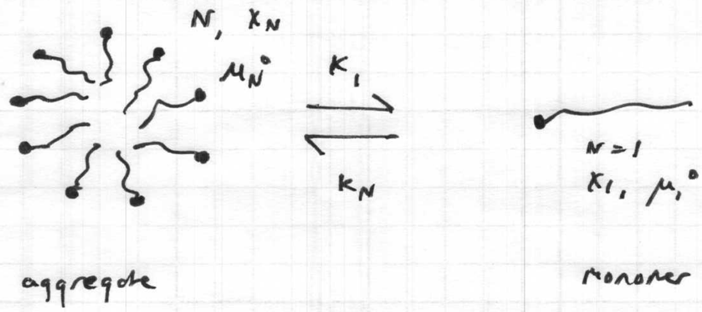
$$C = X_1 + X_2 + X_3 \ldots X_N = \sum_{N=1}^{\infty} X_N$$

in solution, assume we have aggregates of 1, 2, ... N monomers each.

the chemical potential (cp) of all components must be equal,

$$\underbrace{\mu}_{\text{mean cp of an aggregation of 'state' } N} = \underbrace{\mu_N^\circ}_{\text{mean interaction energy per molecule in the aggregate}} + \frac{\overbrace{kT}^{k_b}}{N}\ln\left(\frac{X_N}{N}\right) = \text{constant} = \underbrace{\mu_1^\circ + k_bT\ln\left(X_1\right)}_{N=1,\ \text{monomers.}}$$

we can derive this from the law of mass action between an aggregate of state N and monomers (state 1)



"reaction" $\quad N \cdot X_1 \longrightarrow \left(\frac{X_N}{N}\right)$

equilibrium constant, $\quad K = \frac{\overbrace{k_a}^{\text{association}}}{\underbrace{k_d}_{\text{dissociation}}} = \exp\left(\frac{-\Delta G}{k_bT}\right) = \exp\left(\frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}\right)$

rate of association $= \overbrace{K_1}^{X_1^N} = k_a X_1^N$

rate of dissociation $= K_N \frac{X_N}{N} = k_d \frac{X_N}{N}$

reaction rate constant

$$nA + mB \rightarrow C + D$$

$$\frac{d[C]}{dt} = k(T)[A]^n[B]^m$$

single-step reaction

$$k(T) = Ae^{-Ea/RT}$$

$\Delta G/k_bT$

* see "chemical equilibrium" on wikipedia

In equilibrium, rates of association and dissociation must be equal

hence, $k_a X_1^N = k_d \frac{X_N}{N}$

$$\Longrightarrow K = \frac{k_a}{k_d} = \left(\frac{X_N}{N}\right)\frac{1}{X_1^N} = \exp\left(\frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}\right)$$

log of both sides : $\frac{X_N}{N} = X_1^N \exp\left(\frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}\right)$

$$\ln\left(\frac{X_N}{N}\right) = N \ln X_1 + \frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}$$

mistake as initially uploaded

$$\underline{\Longrightarrow \mu_N^\circ + \frac{\frac{1}{N}\ln\left(\frac{X_N}{N}\right)}{(k_bT)^{-1}} = \frac{\ln X_1}{(k_bT)^{-1}} + \mu_1^\circ}$$

same as stated earlier

relates chemical potentials in aggregation states.

generalize between states N and M.

$$\underbrace{\mu_N^\circ + \frac{\ln(X_N/N)}{M(k_bT)^{-1}}}_{\text{aggregation state } N} = \underbrace{\mu_M^\circ + \frac{\ln(X_M/M)}{M(k_bT)^{-1}}}_{\text{aggregation state } M}$$

solve for $X_N = f(X_M)$, relating state N to M.

$$X_N = N\left\{\left(\frac{X_M}{M}\right)\exp\left(M(\mu_M^\circ - \mu_N^\circ)/k_bT\right)\right\}^{N/M}$$