NM - Self-assembly in solution

- Formation of aggregates ("micelles")

Consider * amphiphilic * molecules (Greek root = "both + friendliness")

\[
\text{ex. } \quad \begin{array}{c}
\text{hydrophilic} \\
\text{hydrophobic}
\end{array}
\]

(in H2O, hydrophobic ends = in core)

So let's consider a solution of amphiphiles, or * generally any polymer * (monomer = one part in assembly of many parts)

Define \( \chi_N \) = dimensionless molar fraction of components (monomers) in solution

as the \( N \)th aggregate. So the concentration of the \( N \)th aggregate is

\[
c_N = \frac{\chi_N}{N}
\]

Total molar fraction of monomers in solution:

\[
c = \chi_1 + \chi_2 + \chi_3 \ldots \chi_N = \sum_{n=1}^{N} \chi_n
\]
in solution, assume we have aggregates of 1, 2, ... N monomers each.

The chemical potential \( \mu \) of all components must be equal,

\[
\mu = \mu^0 + \frac{kT}{N} \ln \left( \frac{N_m}{N} \right) = \text{constant} = \mu^0 + kT \ln \left( \frac{k_1}{N} \right)
\]

mean \( \mu \) of an aggregation of 'state' \( N \) interaction energy per particle in the aggregate

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

\[
N \cdot \mu^0 \xrightarrow{k_1} \frac{N_m}{N} \xrightarrow{k_N} N \cdot \mu^0
\]

rate of association = \( k_1 \cdot k_a \cdot X_i \)

rate of dissociation = \( k_N \cdot X_m = k_d \cdot X_m \frac{N}{N} \)

\[
\frac{d[X]}{dt} = k(T) [A]^N [B]^N
\]

\[
k(T) = A e^{-\frac{E_a}{RT}}
\]

*see "chemical equilibrium" on wikipedia*
In equilibrium, rates of association and dissociation must be equal.

\[ k_a X_1^N = k_d X_N \]

\[ \Rightarrow K = \frac{k_a}{k_d} = \left(\frac{X_N}{X_1^N}\right) = \exp\left(\frac{-N\left(M_N^0 - M_1^0\right)}{k_B T}\right) \]

Log of both sides:

\[ \ln\left(\frac{X_N}{X_1^N}\right) = N \ln X_1^N + \frac{-N\left(M_N^0 - M_1^0\right)}{k_B T} \]

\[ \frac{1}{N} \ln\left(\frac{X_N}{X_1^N}\right) = \frac{\ln X_1^N}{(k_B T)^{-1}} + \frac{M_1^0}{(k_B T)^{-1}} \]

Same as stated earlier.

Generalize between states N and M.

\[ m_N^0 + \frac{\ln\left(\frac{X_N}{X_M}\right)}{M(k_B T)^{-1}} = m_M^0 + \frac{\ln\left(\frac{X_M}{X_N}\right)}{M(k_B T)^{-1}} \]

Solve for \( X_N = f\left(\frac{X_M}{X_N}\right) \), relating state N to M.

\[ X_N = N\left(\frac{X_M}{M}\exp\left(M\left(M_N^0 - M_1^0\right)/k_B T\right)\right)^{N/M} \]
and if \( M = 1 \)

\[
X_N = N \left\{ X_1 \exp \left( \frac{\mu_i^0 - \mu_N^0}{k_B T} \right) \right\}^N 
\]

\[
\sum_{m=1}^{\infty} c = \sum_{m=1}^{\infty} \frac{X_N}{X_1} 
\]

Correctly describes the aggregation states of the system.

Using this model, can we tell when will aggregates form?

When there is a difference in the cohesive energies of the monomers in their dispersed and aggregated states.

If all experience the same interaction with their surroundings, molecules in different sized aggregates

\[
\mu_i^0 = \mu_{i-1}^0 = \mu_N^0 
\]

Our previous result simplifies to \( X_N = N X_1^N \)

Since \( X_1 < 1 \), \( X_N < X_1 \) \( \Rightarrow \) Most molecules are monomers, \( N = 1 \) state

Then for large stable aggregates, we need

\[
\mu_N^0 < \mu_i^0 \text{ for some value of } N 
\]
if $\mu_N^0(N)$ increases with $N$, viz.

then $x_N \ll x_1$ aggregation is even less probable

$= x_N(N)$ is always a distribution function

let's see what it looks like for some key forces and shapes

(i) rods, 1 chains

$\text{bond energy} = \alpha k_b T$

for a $N$ length chain, $N\mu_N^0 = -(N-1)\alpha k_b T$

$\mu_N^0 = -\alpha k_b T + \frac{\alpha k_b T}{N}$

$= \mu_0^0$ relative state to free molecule with bond

$\Rightarrow \mu_N^0 = \mu_0^0 + \frac{\alpha k_b T}{N}$
(2) sticks, \( N \propto \pi R^2 \)
\# of unbound molecules (in edge) \( \propto 2\pi R \propto N^{1/2} \)

\[ \mu_N = \mu^0 + \frac{\alpha kT}{N^{1/2}} \]

(3) spheres, \( N \propto R^2 \)
\# of unbound molecules \( \propto \pi R^2 \propto N^{2/3} \)

\[ \mu_N = \mu^0 + \frac{\alpha kT}{N^{2/3}} \]

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\[ N \mu^0 + \frac{4\pi R^2 \delta}{3} \approx \frac{N}{3} \delta \]

rearrange

\[ \mu_N = \mu^0 + \frac{\delta}{N^{2/3}} \]

\[ \delta \approx \frac{\delta}{N^{2/3}} \]

\[ \alpha = \frac{\frac{4\pi R^2 \delta}{N^{2/3}}}{kT} \]
at which concentration will aggregates form?

\[ \mu_N^* = \mu_m^* + \frac{\alpha kT}{N^p}, \quad p = \text{dimentionless constant} \]

\[ X_N = N \left( x_1 \exp \left( \frac{\mu_m^* - \mu_N^*}{kT} \right) \right) \]

\[ \frac{\mu_1^* - \mu_m^*}{kT} = \alpha \left( 1 - \frac{1}{N^p} \right) \quad (1) \]

To relabel \( X_1 \) to \( X_N \) as before, and substituting \((*)\) there,

\[ X_N = N \left( x_1 \exp \left( \alpha \left( 1 - \frac{1}{N^p} \right) \right) \right)^N \approx N \left( x_1 e^\alpha \right)^N \]

\[ \text{a.g. for spheres, } X_N = \left( x_1 e^\alpha \right)^N e^{-kN} \]

at low \( X_1 \) concentrations such that \( x_1 e^\alpha \ll 1 \), or more precisely \( x_i e^\alpha < N \)

Then \( k_N = k_{N-1} \cdot x_1 \cdot x_2 \ldots \cdot x_i \)

most molecules are monomers in solution.

and \( x_i \approx C \)

when will this change? — well, we can't here

\[ k_N > 1 \]
we cannot have $X_N > 1$, or $X_i > 1$ for that matter

so, returning to $X_N$ as $F(N)$

$$X_1 \text{ cannot exceed } \exp\left( -\frac{(\mu_i - \mu_N)}{k_B T} \right), \text{ else } X_N > 1$$

therefore critical micelle concentration $K_{c,mic}$

$$K_{c,mic} = \exp\left( -\frac{V_i^0 - \mu_i}{k_B T} \right)$$

$$= \exp(-\alpha (1 - \frac{1}{N^p})) \approx e^{-\alpha}$$

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if spheres, recall $\mu_N^0 - \mu_i^0 = \frac{\kappa k_B T}{N^{1/3}} - \alpha k_B T$

$$\mu_i^0 - \mu_N^0 = \kappa k_B T \left( 1 - \frac{1}{N^{1/3}} \right)$$
\[ \mu^{\circ} - \mu^* = \alpha k_b T \left( 1 - \frac{1}{N^{1/3}} \right) \]

\[ \chi_N = N \left\{ \exp \left( \kappa \left( 1 - \frac{1}{N^{1/3}} \right) \right) \right\}^N \]

\[ \chi_N = N \kappa_N e^{-\kappa_N N^{1/3}} \]

\[ e^{\kappa_i} = 1 \Rightarrow \chi_N \approx Ne^{-\kappa N^{1/3}} \]

If \( \alpha > 0 \), then \( \chi_N \) decreases with \( N \) below \( \text{cmc} \).

\[ \text{leads to a large aggregate in solution, which forms rapidly} \]

\[ \text{phase separation, like oil and water, above the \( \text{cmc} \)} \]

However, some systems lead to a particular size distribution, rather than simply phase separating.

Now, what if

\[ \Delta N = N - M \]

expands about \( M \): 

\[ \frac{\mu^N - \mu^M}{M} = \Lambda (\Delta N)^2 \]

(particular form)

\[ \chi_N = N \left\{ \frac{\kappa M}{N^M} \exp \left( \frac{-M \Lambda (\Delta N)^2 k_b T}{1} \right) \right\}^{N/M} \]

Gaussian distribution is \( \chi \exp \left( -\frac{(x-\bar{x})^2}{2\sigma^2} \right) \)

becomes an aggregate of certain size is stable,

\( \text{non-symmetric interactions} \)
Now we can plot the distribution,

\[ KN \]

or can also are better care.

\[ N \]

So using standard gaussian form, \( \Delta N = x - \bar{x} = N - N \)

\[ 2\sigma^2 = \frac{K_B T}{N \Lambda} \]

\[ \sigma = \sqrt{\frac{K_B T}{2N \Lambda}} \sim \text{order of aggregation} \]

* More shape/curvature effects to be explored later.