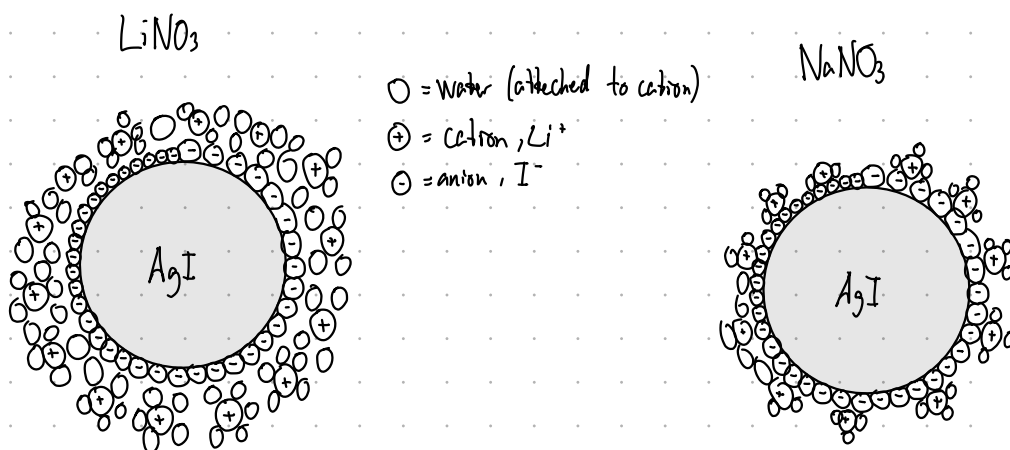


Exercise 1:

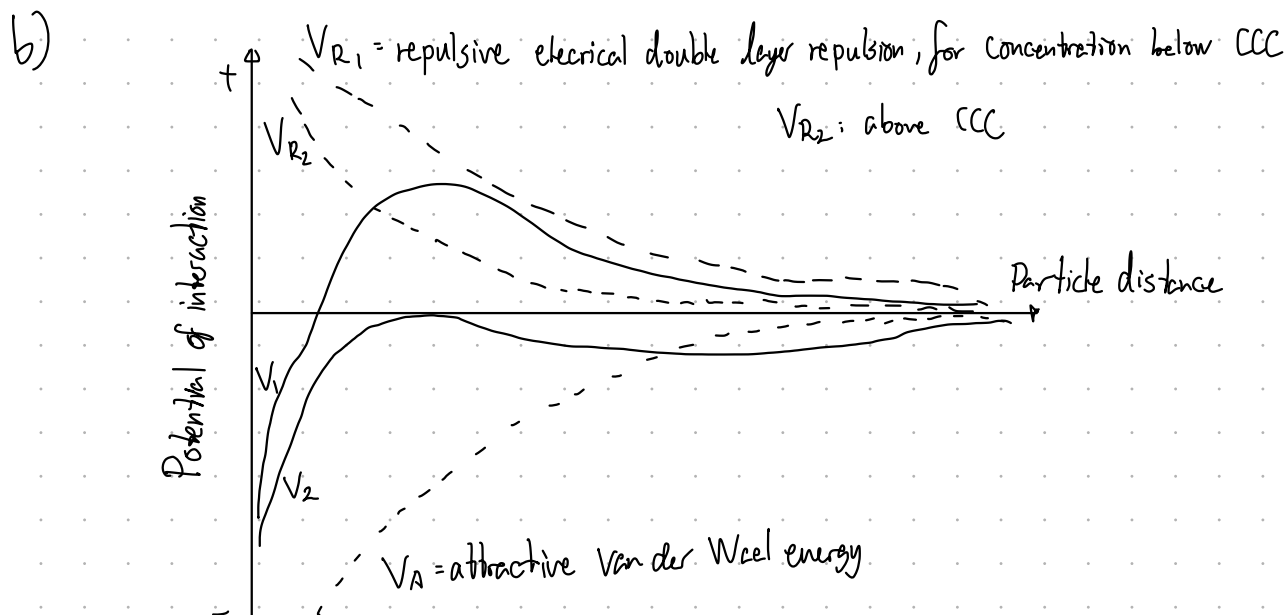
- A dispersion of negatively charged AgI particles is prepared using two different aqueous electrolyte solutions at 25°C: a) LiNO₃ (165) and b) NaNO₃ (140). The critical coagulation concentration (CCC) is given in parenthesis in mmol/l. For each electrolyte solution draw one particle and its immediate ionic environment, indicating the co-ions and counterions. Explain what the CCC is and why the CCC value of LiNO₃ is higher than that of NaNO₃.
- Draw the potential energy curves for two particles approaching each other in the case when the electrolyte concentration is above CCC and in the case when the electrolyte concentration is below CCC. Which of the two conditions would you describe as stable?

a) CCC is the minimum electrolyte concentration necessary for a dispersion to coagulate

The reason why the CCC of LiNO₃ is higher than NaNO₃ is that Li is more lyotropic (Hofmeister series), and is more easily hydrated. This means that in order to have coagulation, it will take more Li-ions than Na-ions. Which in turn is why Li has the highest CCC



The Li⁺ ions are further from the stern layer due to having more water molecules attached to it than Na⁺ ions



V1 is when the electrolyte concentration is below CCC, there is an energy barrier preventing coagulation.

V2 is when the electrolyte concentration is above CCC, the energy barrier (from the secondary minimum) is quite small, and the potential is negative, which means that particles will spontaneously move closer to each other, causing coagulation.

Based on this, the system with an electrolyte concentration below CCC (V1), is the most stable.

Exercise 2 (or NEW):

Colloidal gold particles dispersed in water at 20°C were flocculated by adding NaCl. The radius of the gold particles was $R_s = 3,69 \text{ nm}$. The number of particles were experimentally determined at different times, as shown in the Table below:

t (s)	120	195	270	390	450
N (cm ⁻³)	$11,2 \times 10^8$	$7,3 \times 10^8$	$5,4 \times 10^8$	$4,5 \times 10^8$	$3,7 \times 10^8$

Determine the second-order rate constant k_{exp} that describes the flocculation process.

Calculate the stability ratio (W).

Based on W, what can you say about the stability of the dispersion?

$$k_B = 1,38 \times 10^{-23} \text{ J/K}$$

$$\eta = 10^{-3} \text{ kg/ms}$$

Fast coagulation: $\frac{dN}{dt} = -k_2 N^2$

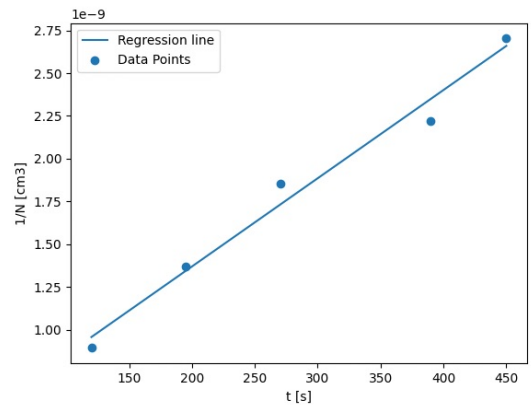
$$\int_{N_0}^N \frac{dN}{N^2} = \int k_2 dt$$

$$\left[\frac{1}{N} \right]_{N_0}^N = k_2 t$$

$$\frac{1}{N} - \frac{1}{N_0} = k_2 t$$

$$\frac{1}{N} = k_2 t + \frac{1}{N_0}$$

Plot $\frac{1}{N}$ against t , slope = $k_2 = 5,2 \cdot 10^{-12} \text{ cm}^3/\text{s}$



$$W = \frac{k_2^0}{k_2}$$

$$k_2^0 = \frac{4 k_B T}{3 \eta}$$

$$k_2^0 = \frac{4 k_B T}{3 \eta} = \frac{4 \cdot 1,38 \cdot 10^{-23} \text{ J/K} \cdot 293 \text{ K}}{3 \cdot 10^{-3} \text{ kg/ms}} = 5,4 \cdot 10^{-18} \text{ m}^3/\text{s} = 5,4 \cdot 10^{-12} \text{ cm}^3/\text{s}$$

$$W = \frac{k_2^0}{k_2} = \frac{5,4 \cdot 10^{-12} \text{ cm}^3/\text{s}}{5,2 \cdot 10^{-12} \text{ cm}^3/\text{s}} = 1,038$$

W is quite close to 1, when W is 1, the concentration of electrolytes in the solution is at CCC. This means that the system is very close to coagulating, therefore it is unstable.

Exercise 3:

The number of oil droplets in an emulsion is measured to $9,5 \times 10^{15}$ droplets/m³ and average radius is $0,05 \mu\text{m}$. The droplets are stabilised by an anionic surfactant Na^+R^- with a bulk concentration of $1,5 \times 10^{-3} \text{ mol/dm}^3$.

NaNO_3 is added to the emulsion, resulting in a concentration of $0,004 \text{ mol/dm}^3$.

After 60 minutes the number of droplets were reduced to $8,9 \times 10^{15}$ droplets/m³.

$$T = 25^\circ\text{C}$$

$$k_B = 1,38 \times 10^{-23} \text{ J/K}$$

$$\eta = 8,9 \times 10^{-4} \text{ kg/ms}$$

a. Determine the second-order rate constant (k_{exp}) that describes the flocculation process. Calculate the stability factor W

b. If the resulting concentration is $0,01 \text{ mol/dm}^3$ upon NaNO_3 addition, the stability factor is $W = 1,9$.

Use the following three relationships to verify that the surface potential (ψ_0) is -32 mV :

$$\log W = K_1 \log c + K_2, \quad K_1 = \left[\frac{-2,15 \times 10^9 T_0^2 R_s}{z^2} \right], \quad T_0 = \frac{[\exp(\frac{ze\psi_0}{2k_B T}) - 1]}{[\exp(\frac{ze\psi_0}{2k_B T}) + 1]}$$

$$e = 1,6 \times 10^{-19} \text{ C}$$

a) Using the expressions from problem 2

$$\frac{1}{N} - \frac{1}{N_0} = k_2 t$$

$$\Rightarrow k_2 = \frac{\frac{1}{N} - \frac{1}{N_0}}{t} = \frac{\frac{1}{8,9 \cdot 10^{16} \text{ m}^{-3}} - \frac{1}{9,5 \cdot 10^{15} \text{ m}^{-3}}}{60 \cdot 60 \text{ s}}$$

$$\underline{k_2 = 1,97 \cdot 10^{-21} \text{ m}^3/\text{s}}$$

$$k_2^0 = \frac{4k_B T}{3\eta} = \frac{4 \cdot 1,38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}{3 \cdot 8,9 \cdot 10^{-4} \text{ kg/ms}}$$

$$\underline{k_2^0 = 6,16 \cdot 10^{-16} \text{ m}^3/\text{s}}$$

$$\underline{W = \frac{k_2^0}{k_2} = \frac{6,16 \cdot 10^{-16} \text{ m}^3/\text{s}}{1,97 \cdot 10^{-21} \text{ m}^3/\text{s}} = 3127}$$

b) We end up with 2 datapoints, and can determine K_1 and K_2

$$\text{With } c_{\text{NaNO}_3} = 0,004 \text{ M}, \quad c_{\text{tot}} = 1,5 \cdot 10^{-3} \text{ M} + 0,004 \text{ M} = 5,5 \cdot 10^{-3} \text{ M}$$

$$\log 3127 = K_1 \cdot \log (5,5 \cdot 10^{-3}) + K_2$$

$$\text{With } c_{\text{NaNO}_3} = 0,01 \text{ M}, \quad c_{\text{tot}} = 0,01 \text{ M} + 1,5 \cdot 10^{-3} \text{ M} = 0,0115$$

$$\log (1,9) = K_1 \cdot \log (0,0115) + K_2$$

Solving for K_1 and K_2 gives:

$$K_1 = -10,04$$

$$K_2 = -44,19$$

Rewriting the given equation:

$$T_0 = \sqrt{\frac{K_1 z^2}{-2,15 \cdot 10^9 \cdot R_5}} = \sqrt{\frac{-10,04 \cdot (-1)^2}{-2,15 \cdot 10^9 \cdot 0,05 \cdot 10^{-6}}} = \underline{\underline{0,31 \text{ K}}}$$

If the provided expression gives the same answer, then it is verified:

$$T_0 = \frac{[\exp(\frac{ze\psi_0}{2k_B T}) - 1]}{[\exp(\frac{ze\psi_0}{2k_B T}) + 1]} = \frac{\exp\left(\frac{(-1) \cdot 1,6 \cdot 10^{-19} \text{ C} \cdot (-32 \cdot 10^{-3} \text{ V})}{2 \cdot 1,38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}\right) - 1}{\exp\left(\frac{(-1) \cdot 1,6 \cdot 10^{-19} \text{ C} \cdot (-32 \cdot 10^{-3} \text{ V})}{2 \cdot 1,38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}\right) + 1} = \underline{\underline{0,3 \text{ K}}} \quad \text{Close enough, most likely a rounding error.}$$

Exercise 4:

An aqueous dispersion of negatively charged gold particles contains $6,3 \times 10^{16}$ particles/dm³. The radius of the particles is $R_s = 10,3 \text{ nm}$. The coagulation kinetics was investigated by adding various amounts of $\text{Na}^+\text{ClO}_4^-$ at 25°C . The following relationship between the electrolyte concentration and the stability factor was found:

c (mol/dm ³)	0,002	0,003	0,005	0,008
W	48	31	17	8,9

- What is the half-time ($t_{1/2}$) of the dispersion if $c = 0,002 \text{ mol/dm}^3$?
- Evaluate the reason for the resulting value of the half-time

a) Using the expressions from problem 2, assuming $\eta = 8,9 \cdot 10^{-4} \text{ kg/ms}$ (Blackboard announcement)

$$k_2^0 = \frac{4k_B T}{3\eta} = \frac{4 \cdot 1,38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}{3 \cdot 8,9 \cdot 10^{-4} \text{ kg/ms}}$$

$$\underline{k_2^0 = 6,16 \cdot 10^{-16} \text{ m}^3/\text{s}}$$

$$W = \frac{k_2^0}{k_2} \Rightarrow k_2 = \frac{k_2^0}{W} = \frac{6,16 \cdot 10^{-16} \text{ m}^3/\text{s}}{48} = 1,28 \cdot 10^{-19} \text{ m}^3/\text{s}$$

$$\boxed{\frac{1}{N} = k_2 t - \frac{1}{N_0}} \quad \text{At } t_{1/2}, N = 0,5 N_0$$

$$\Rightarrow t_{1/2} = \frac{1}{k_2} \left(\frac{1}{0,5 N_0} - \frac{1}{N_0} \right) = \frac{1}{k_2} \cdot \frac{1}{N_0}$$

$$t_{1/2} = \frac{1}{k_2 \cdot N_0} = \frac{1}{1,28 \cdot 10^{-19} \text{ m}^3/\text{s} \cdot 6,3 \cdot 10^{16} (\text{dm}^3)^{-1}} = 124 \text{ s} \cdot \frac{\text{dm}^3}{10^3 \text{ m}^3} = 0,124 \text{ s}$$

$$\underline{\underline{t_{1/2} = 0,124 \text{ s}}}$$

b)

The half-time is low.

This is most likely due to high concentrations of both gold particles and electrolyte, as well as the surface potential of the gold particles having a quite low value. This causes rapid spontaneous coagulation.

Exercise 5:

A biotechnology company produces industrial enzymes by fermentation on a large scale. After the fermentation with enzyme-producing microorganisms, the biomass (i.e. the living cells) are killed using heat treatment and high pH. The dead biomass is removed from the enzyme-containing liquid by coagulation or flocculation followed by centrifugation. The moist biomass is finally sold as fertilizer to farmers.

The coagulation/flocculation process takes place in a so-called thickener using the coagulation agent CaCl_2 and adjustment of pH. The concentration of CaCl_2 used in the thickener is 100 mM. The thickener liquid has a viscosity of $10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$, a density of 1000 kg m^{-3} , a relative permittivity of 80.2 and a Hamaker constant (in vacuum) of $3.7 \times 10^{-20} \text{ J}$. The temperature is 20°C . The individual cells can be assumed to be spherical, rigid and have a diameter of $1 \mu\text{m}$. The Hamaker constant (in vacuum) of the cells considered is $6 \times 10^{-20} \text{ J}$. The cell surface (phospholipid membrane) zeta potential, at the pertinent pH, is assumed constant at all times and equal to -15 mV . Any potential influence of steric stabilisation and retardation effects can be neglected.

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/\text{Jm}$$

- Calculate the composite (overall) interaction energy between two cells in the thickener when the closest distance between the surfaces of the particles is 0.1, 1, 2, 5, 10 and 25 nm. Comment on the stability of the cell dispersion.
- For economic reasons, it is suggested to replace CaCl_2 by MgCl_2 as coagulation agent and use the new salt at the same concentration as CaCl_2

was used in the thickener. Explain how this can be expected to affect the efficiency of the coagulation process.

- Provide a crude estimate of the critical coagulation concentration of MgCl_2 . Comment on the result.

$$a) \quad A_{12} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

$$A_{123} = (A_{11}^{1/2} - A_{22}^{1/2})(A_{33}^{1/2} - A_{22}^{1/2})$$

Need A_{121}

$$A_{121} = (A_{11}^{1/2} - A_{22}^{1/2})(A_{11}^{1/2} - A_{22}^{1/2}) = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

$$A_{121} = ((6 \cdot 10^{-20})^{0.5} - (3.7 \cdot 10^{-20})^{0.5})^2 = 2.77 \cdot 10^{-21} \text{ J}$$

$$V_A \text{ for spheres: } V_A = - \frac{A \cdot R}{12 \cdot H} = \frac{2.77 \cdot 10^{-21} \text{ J} \cdot 0.5 \cdot 10^{-6} \text{ m}}{12 \cdot H} = \frac{1.15 \cdot 10^{-26} \text{ Jm}}{H}$$

This eq was used to fill out the table further below

V_R , must evaluate $K \cdot R_s$

Ions: Ca^{2+} , $z=+2$, $[\text{Ca}^{2+}] = 0.1 \text{ M}$
 Cl^- , $z=-1$, $[\text{Cl}^-] = 0.2 \text{ M}$

$$K = \sqrt{\frac{1000 e^2 N_A}{\epsilon_k \epsilon_0 T}} \cdot \sum z_i^2 C_i$$

$$\sum z_i^2 C_i = 2^2 \cdot 0.1 + (-1)^2 \cdot 0.2 = 0.6$$

$$K = \sqrt{\frac{1000 \cdot \frac{\text{C}^2}{\text{Jm}} \cdot (1.6 \cdot 10^{-19} \text{ C})^2 \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1}}{80.2 \cdot 8.854 \cdot 10^{-12} \text{ C}^2/\text{Jm} \cdot 1.38 \cdot 10^{-23} \text{ J/K} \cdot 293 \text{ K}}} \cdot 0.6 \frac{\text{mol}}{\text{dm}^3} = 1.795 \cdot 10^9 \text{ m}^{-1}$$

(Eq. 9.5 in Mark)

$$K \cdot R_s = 1.795 \cdot 10^9 \text{ m}^{-1} \cdot 0.5 \cdot 10^{-6} \text{ m} = 897 \gg 1 \Rightarrow V_R = 2\pi \epsilon R_s \psi_0^2 \ln(1 + \exp(-K \cdot H))$$

Using $\epsilon = \epsilon_r \epsilon_0 = 80 \cdot 8,854 \cdot 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$

$R_0 = 0,5 \mu\text{m}$

$\psi_0 = -15 \cdot 10^{-3} \text{ V}$

We get V_R in the table

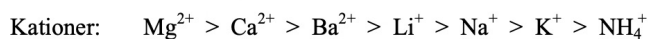
Then: $V_{\text{tot}} = V_A + V_R$, using a script we get:

H [nm]	V_A [J]	V_R [J]	Total [J]
0,1	$-1,15 \cdot 10^{-18}$	$3,05 \cdot 10^{-19}$	$-8,48 \cdot 10^{-19}$
1	$-1,15 \cdot 10^{-19}$	$7,71 \cdot 10^{-20}$	$-3,81 \cdot 10^{-20}$
2	$-5,76 \cdot 10^{-20}$	$1,37 \cdot 10^{-20}$	$-4,40 \cdot 10^{-20}$
5	$-2,31 \cdot 10^{-20}$	$6,35 \cdot 10^{-23}$	$-2,30 \cdot 10^{-20}$
10	$-1,15 \cdot 10^{-20}$	$8,05 \cdot 10^{-27}$	$-1,15 \cdot 10^{-20}$
25	$-4,61 \cdot 10^{-21}$	0	$-4,61 \cdot 10^{-21}$

All of the interaction energies are negative, this means that coagulation will happen spontaneously, as there is no positive energy barrier preventing coagulation. The cell dispersion is therefore unstable.

b)

The tendency of different ions to become hydrated varies strongly. Thus, anions and cations can be arranged in a lyotropic ("solvent seeking") series of decreasing salting-out power, a so-called Hofmeister series:



Looking at the Hofmeister series, magnesium ions are more easily dissolved into the solvent than calcium ions, and therefore, Mg-ions will interact less with the cells in the solution than the Ca-ions.

This means that there will be less "shielding" of the repulsive forces between the cells, causing MgCl_2 to be a worse coagulation agent than CaCl_2 .

The coagulation will be slower and/or less of the cells will coagulate.

c)

From table 10,4: $\frac{1}{K} = \frac{0,176}{\sqrt{CCC}} \Rightarrow CCC = (0,176 \cdot K)^2 = \underline{\underline{0,0998 \text{ M}}}$

As MgCl_2 is a worse coagulation agent than CaCl_2 , it is expected that the CCC of the MgCl_2 -system is higher.