

Exercise 1:

- What are the main stabilisation mechanisms for colloidal dispersions?
- What is bridging flocculation?
- Explain how non-ionic polymers that form a "brushlike" layer on particles can stabilise dispersions.
- Colloidal particles in wastewater, left for several days, do not flocculate when the water contains 0,1 mole/l calcium chloride. What is the likely stabilisation mechanism for the particles?

a) The main stabilization mechanisms are electrostatic and steric stabilization, if both of the mechanisms are present in a dispersion, it is called electrostatic stabilization. We also have particle stabilization

b) Bridging flocculation is when a polymer is adsorbed on two particles (at different parts of the chain), creating a bridge between the particles.

c) This is a form of steric stabilization. The lyophobic part of the polymer attaches to the particle surface, at high enough concentrations of polymers, this causes the formation of a brushlike layer. This layer prevents the particles from coagulating by steric hindrance, which stabilizes the dispersion.

d) The extension of the electrical double layer decreases with increasing ionic strength. In this system, the ionic strength is 0.6 M. Which is quite large. This means that the electrical double layer does not extend much. This means that the electrostatic repulsion does not take effect until the particles are close, at which point the attractive forces will be large. Most likely causing flocculation or coagulation. As the solution does not flocculate for several days, in this case, the stabilization mechanism is most likely steric stabilization.

Exercise 2:

A particular product is an o/w emulsion and is based on equal amounts (weight percent) of two surfactants, which are both hydrophilic. The first surfactant has a HLB = 13 and the other has a HLB = 11.

The company where you are currently working wishes, for various reasons, to change the formulation of the surfactants used for the stabilisation of this o/w emulsion product. Of course, the product must have the same o/w emulsion characteristics.

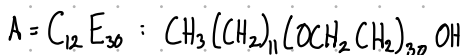
This time the company suggests using a mixture of hydrophobic and hydrophilic surfactants, both of which are non-ionic and belong to the family of poly(oxyethylene alcohols)s, known as poly(ethylene oxide)s. The research director suggests using the surfactants C₁₂E₃₀ and C₁₆E₆ (see Table below). The formulation is, thus, based on both hydrophilic and hydrophobic surfactants. How much (weight) percentage of the new hydrophilic surfactant is needed for this specific o/w emulsion?

Category	Name	Structure
Anionic	Sodium stearate	CH ₃ (CH ₂) ₁₆ COO ⁻ Na ⁺
	Sodium oleate	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COO ⁻ Na ⁺
	Sodium dodecyl sulfate (SDS)	CH ₃ (CH ₂) ₁₁ SO ₄ ⁻ Na ⁺
	Sodium dodecyl benzene sulfonate	CH ₃ (CH ₂) ₁₁ C ₆ H ₄ SO ₃ ⁻ Na ⁺
Cationic	Dodecylamine hydrochloride	CH ₃ (CH ₂) ₁₁ NH ₃ ⁺ Cl ⁻
	Hexadecyl(trimethyl)ammonium bromide (CTAB)	CH ₃ (CH ₂) ₁₅ N(CH ₃) ₃ ⁺ Br ⁻
Non-ionic	Polyethylene oxides (C _x E _y or C _x EO _y)	CH ₃ (CH ₂) _{x-1} (OCH ₂ CH ₂) _y OH
	Nonylphenyl ethoxylates (λ _{EO} is the number of ethylene oxide groups)	CH ₃ (CH ₂) ₈ -C ₆ H ₄ -(OCH ₂ CH ₂) _{λ(EO)} OH

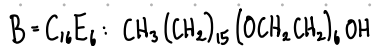
Table 11.5 HLB numbers of molecular groups

Chemical group	HLB	Chemical group	HLB
-SO ₄ Na	38.7	-O-	1.3
-COOK	21.1	-OH (sorbitan)	0.5
-COONa	19.1	-(CH ₂ -CH ₂ -O)-	0.33
-SO ₃ Na	11.0	-(CH ₂ CH ₂ CH ₂ O)-	-0.15
-N (tertiary amin)	9.4	-CH ₂ -	-0.475
Ester (sorbitan ring)	6.8	-CH ₃	-0.475
Phenol residue, -C ₆ H ₄ -O-	~ 6.5	=CH ₂ -	-0.475
Free ester group	2.4	-CF ₂ -	-0.87
-COOH	2.1	-CF ₃	-0.87
-OH	1.9		

$$HLB_{mix}^0 = 0,5 \cdot 11 + 0,5 \cdot 13 = 12$$



$$HLB_A = 7 + 1(-0,475) + 11(-0,475) + 30 \cdot 0,33 + 1,9 = 13,1$$



$$HLB_B = 7 + 1 \cdot (-0,475) + 15 \cdot (-0,475) + 6 \cdot 0,33 + 1,9 = 3,28$$

$$HLB_{mix} = W_A \cdot HLB_A + (1 - W_A) \cdot HLB_B$$

$$= W_A (HLB_A - HLB_B) + HLB_B$$

$$\Rightarrow W_A = \frac{HLB_{mix} - HLB_B}{HLB_A - HLB_B} = \frac{12 - 3,28}{13,1 - 3,28} = \underline{\underline{88,8\%}}$$

Exercise 3:

An optimal HLB for an emulsion product is reported to be 10.3.

a. What type of emulsion do we have?

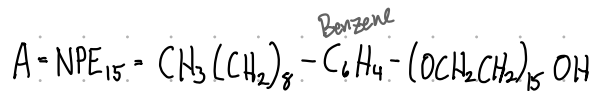
a) As $HLB > 8$, we have an o/w emulsion

Suddenly, one of the hydrophilic surfactants you are using in your company for this specific formulation is no longer available in the market. The hydrophobic surfactant (with $HLB = 2.1$) is still available and it is very cheap (irrespective of the amount employed). Researchers from the research department of your company suggest three possibilities: i) a secret "in-house" (possibly anionic) surfactant X which has an oil-water partition coefficient equal to 2×10^9 (they do not reveal the structure); ii) NPE₁₅ and NPE₃₀ (NPE = nonyl phenyl ethoxylates where the subscript is the number of ethylene oxide groups). The management department informs you that the cost of these three surfactants is almost the same.

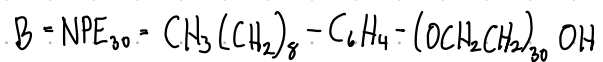
b. Which one of the three surfactants (X, NPE₁₅ or NPE₃₀) would you recommend to your manager for this specific product as a substitute for the surfactant that is no longer on the market?

Category	Name	Structure
Anionic	Sodium stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$
	Sodium oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}^-\text{Na}^+$
	Sodium dodecyl sulfate (SDS)	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+$
	Sodium dodecyl benzene sulfonate	$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3^-\text{Na}^+$
Cationic	Dodecylamine hydrochloride	$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+\text{Cl}^-$
	Hexadecyl(trimethyl)ammonium bromide (CTAB)	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3^+\text{Br}^-$
Non-ionic	Polyethylene oxides (C_nE_m or C_nEO_m)	$\text{CH}_3(\text{CH}_2)_{n-1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$
	Nonylphenyl ethoxylates (X_{EO} is the number of ethylene oxide groups)	$\text{CH}_3(\text{CH}_2)_8\text{-C}_6\text{H}_4\text{-(OCH}_2\text{CH}_2)_{\text{X(EO)}}\text{OH}$

$$b) HLB_x = 7 + 0.36 \cdot \ln(K_{o/w}) = 14.71$$



$$HLB_A = 7 + 9 \cdot (-0.475) + 6 \cdot (-0.475) + 15 \cdot 0.33 + 1.9 = 6.725$$



$$HLB_B = 7 + 9 \cdot (-0.475) + 6 \cdot (-0.475) + 30 \cdot 0.33 + 1.9 = 11.675$$

NPE₃₀ is the best substitute

Exercise 4:

A surfactant foam has a liquid/air surface tension of 25 mN/m. Bubbles in the foam can be assumed to be spherical and monodisperse with a diameter of 20 μm . The Hamaker constant for the air/liquid/air interface can be taken to be 6×10^{-20} J. Calculate the critical film rupture thickness.

$$\frac{J \cdot \text{m}^2}{\text{N} \cdot \text{Pa}} = \text{m}^2$$

$$h_c = 0.207 \left(\frac{A_{121}^2 R_B^2}{\gamma_{AL} \cdot \Delta P} \right)^{1/7} = 0.207 \cdot \left(\frac{(6 \cdot 10^{-20} \text{ J})^2 \cdot (10 \cdot 10^{-6} \text{ m})^2}{25 \cdot 10^{-3} \text{ N/m} \cdot 5000 \text{ Pa}} \right)^{1/7} = 1.247 \cdot 10^{-8} \text{ m} = \underline{\underline{12.47 \text{ nm}}}$$

$$\text{Young's eq: } \Delta P = \gamma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = 25 \cdot 10^{-3} \text{ N/m} \cdot 2 \cdot \frac{1}{10 \cdot 10^{-6} \text{ m}} = 5000 \text{ Pa}$$

$R_1 = R_2 = R_3$

Exercise 5:

A newly formed foam with a liquid/air surface tension of 40 mN/m and bubble diameter of 2 mm is exposed to draining by gravity. It can be assumed that the draining corresponds to that of a vertical water film of uniform thickness. Density and viscosity of the liquid phase can be taken to 1000 kg/m³ and 10⁻³ kg/ms, respectively.

- What is the average rate of vertical draining when the film is 100 and 10 nm thick, respectively?
- How can the rate of draining by gravity be reduced?

The foam is also exposed to horizontal draining.

- What is the rate of horizontal draining for a film of thickness 110 nm and a radius, R_f , equal to 0.1 mm?
- How can the rate of draining by capillary forces be reduced?

$$a) V_{AV} = \frac{g \cdot \gamma_L \cdot \delta(t)^2}{8 \eta_L}$$

$$100 \text{ nm: } V_{AV} = \frac{9.81 \text{ m/s}^2 \cdot 1000 \text{ kg/m}^3 \cdot (100 \cdot 10^{-9} \text{ m})^2}{8 \cdot 10^{-3} \text{ kg/ms}} = 12.26 \text{ nm}$$

$$10 \text{ nm: } V_{AV} = \frac{9.81 \text{ m/s}^2 \cdot 1000 \text{ kg/m}^3 \cdot (10 \cdot 10^{-9} \text{ m})^2}{8 \cdot 10^{-3} \text{ kg/ms}} = 0.1226 \text{ nm}$$

b) Choose a liquid phase with a lower density, and a higher viscosity.

$$c) \quad \frac{d\delta}{dt} = - \frac{2\delta^3 \Delta P}{3\eta_L R_f^2} = - \frac{2 \cdot (110 \cdot 10^{-9} \text{ m})^3 \cdot 80 \text{ Pa}}{3 \cdot 10^{-3} \text{ kg/s} \cdot (0.1 \cdot 10^{-3} \text{ m})^2} = - 7,10 \text{ nm/s}$$

$$\Delta P = \frac{2\gamma_{AL}}{R_B} = \frac{2 \cdot 40 \cdot 10^{-3} \text{ N/m}}{1 \cdot 10^{-3} \text{ m}} = 80 \text{ Pa}$$

d) We can reduce the rate of draining by choosing a different liquid phase with a lower viscosity and/or a higher interfacial tension with air.

Exercise 6:

The following data are available for a foam made by use of the flotation frother (surfactant) methyl isobutyl carbinol: $c = 20 \text{ mol/m}^3$, $\Gamma_m = 5 \times 10^{-6} \text{ mol/m}^2$, $K_L = .23 \text{ m}^3/\text{mol}$, $\delta = 20 \text{ nm}$. The temperature is 20°C .

The Langmuir-Szyszkowski equation is valid for adsorption of the surfactant:

$$\gamma = \gamma_0 - R_{ig} T \Gamma_m \ln(1 + K_L c)$$

- Calculate the surface elasticity of the foam.
- Calculate the equilibrium adsorption density of the surfactant.

Hint: Use the equation to find γ and use the obtained value to find Γ (assuming linearity). Use the surface tension of pure water as 72 mN/m

$$a) \quad E = \frac{4R_{ig} T \Gamma_m^2 K_L^2 \cdot c}{\delta(1 + K_L c)^2 + 2\Gamma_m K_L}$$

$$E = \frac{4 \cdot 8,314 \text{ J/mol} \cdot \text{K} \cdot 293 \text{ K} \cdot (5 \cdot 10^{-6} \text{ mol/m}^2)^2 \cdot (0,23 \cdot \text{m}^3/\text{mol})^2 \cdot 20 \text{ mol/m}^3}{20 \cdot 10^{-9} \text{ m} \cdot (1 + 0,23 \text{ m}^3/\text{mol} \cdot 20 \text{ mol/m}^3)^2 + 2 \cdot 5 \cdot 10^{-6} \text{ mol/m}^2 \cdot 0,23 \text{ m}^3/\text{mol}} = 88 \text{ mN/m}$$

b) Using the Gibbs adsorption isotherm: $\Gamma_2 = - \frac{1}{nRT} \left(\frac{d\gamma}{d \ln c} \right)_T$
Non-dissociating surfactant $n=1$

$$\Gamma_2 = - \frac{1}{RT} \left(\frac{d\gamma}{d \ln c} \right)_T = - \frac{c}{RT} \left(\frac{d\gamma}{dc} \right)_T$$

$$\frac{d \ln c}{dc} = \frac{1}{c} \Rightarrow \frac{1}{d \ln c} = \frac{c}{dc}$$

Assuming linearity: $\Gamma_2 = - \frac{c}{RT} \frac{\Delta\gamma}{\Delta c}$

$$\Delta\gamma = \gamma - \gamma_0 = \gamma_0 - R_{ig} T \Gamma_m \ln(1 + K_L c) - \gamma_0 = - R_{ig} T \Gamma_m \ln(1 + K_L c)$$

$$\Delta c = c - c_0 = c - 0 = c$$

$$\Rightarrow \Gamma_2 = - \frac{c}{RT} \cdot \frac{- R_{ig} T \Gamma_m \ln(1 + K_L c)}{c} = \Gamma_m \cdot \ln(1 + K_L c)$$

$$\Gamma_2 = 5 \cdot 10^{-6} \text{ mol/m}^2 \cdot \ln(1 + 0,23 \text{ m}^3/\text{mol} \cdot 20 \text{ mol/m}^3)$$

$$\Gamma_2 = 8,61 \cdot 10^{-6} \text{ mol/m}^2$$

$$\Gamma_2 = 8,61 \text{ } \mu\text{mol/m}^2$$

Exercise 7:

One way to measure emulsion stability is through microfluidic methods. Here, monodisperse droplets, ca. 60 μm in diameter, are continuously generated at a rate of ca. 550 drops/s. During flow, some drops collide and undergo coalescence. High-speed recordings are taken at different points of a long channel (i.e. at increasing residence times) to determine the number of remaining initial-sized drops. The distance between each segment is 33 mm. The total flow rate is equal to 85 $\mu\text{L}/\text{min}$, while the droplets flow at a velocity of 40 mm/s.

Segment	Remaining number of initial-sized drops [1/s]	
	System A	System B
1 (t=0)	550 drop/s	550 drop/s
2	521 drop/s	401 drop/s
3	502 drop/s	366 drop/s
4	486 drop/s	329 drop/s
5	471 drop/s	292 drop/s
6	457 drop/s	246 drop/s

- Calculate the number of drops in 1 ml of generated emulsion and plot the values for both systems as $1/N$ vs time, where N is the number of drops in 1 ml.
- Calculate the second-rate constant (k_{exp}) for both systems.
- Which system is more likely to be stabilized by a surfactant and why?
- Typical rapid coagulation constant should be in the order of $10^{-12} \text{ cm}^3/\text{s}$. Suggest reasons for the difference between the calculated rate constants and this reference value.

b) Using linear regression, and finding the slope of the lines, we get:

$$k_{\text{exp}, A} = 1.239728157840829 \cdot 10^{-7} \text{ mL/s}$$

$$k_{\text{exp}, B} = 7.032669304299234 \cdot 10^{-7} \text{ mL/s}$$

$$\text{mL/s} = 10^{-3} \cdot \text{dm}^3/\text{s} = \text{cm}^3/\text{s}$$

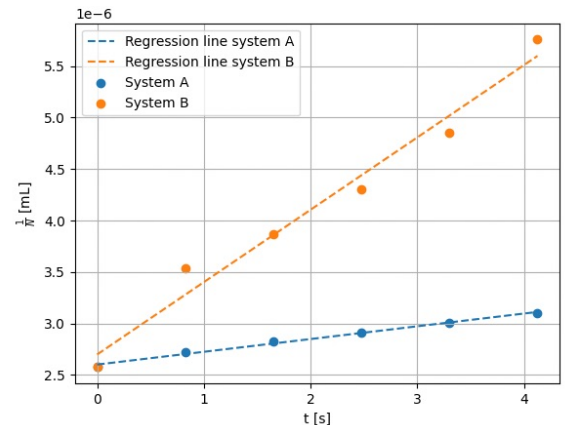
a) The time it takes to create 1 mL:

$$t = \frac{V}{\dot{V}} = \frac{1 \text{ mL}}{85 \mu\text{L}/\text{min}} = 11,76 \text{ min} \approx 706 \text{ s}$$

Multiplying with these numbers gives the number of drops/mL

Time between each segment:

$$t = \frac{\text{distance}}{v_{\text{drops}}} = \frac{33 \text{ mm}}{40 \text{ mm/s}} = 0,825 \text{ s}$$



	Remaining number of droplets					
System A	[388235.	367765.	354353.	343059.	332471.	322588.]
System B	[388235.	283059.	258353.	232235.	206118.	173647.]

- c) Most likely system A, the coalescence is slower than in system B. This suggests that there are repulsive forces in system A, which is probably due to surfactants embedded in the droplets.

d) Usually, we are looking at particles when we are analyzing coagulation, not droplets that are undergoing coalescence. The coalescence between droplets happens «easier» than particles, as droplets merge into larger droplets, which reduces the total surface area. As particles only stick together, the reduction is smaller, meaning the driving force of the coagulation is lower than that of coalescence.

We are looking at systems in flow. Which means that there are more collisions between droplets than there would have been in a dispersion «at rest».

The droplets are larger than the particles we have looked at earlier (Radius of $3 \cdot 10^{-5}$ vs. 10^{-7}). According to the Mørk textbook, the rate of coagulation of large particles can be 10^4 times larger than for smaller particles, so we can assume that the rate of coagulation/coalescence increases with increasing particle/drop size. (At least while using the coagulation model)