

Prof. Paul Bowen
Dr. Andrea Testino
2021

Exercises 9

1. **What are the different forces (attractive and repulsive) that could act between the particles of a powder suspension? What are their origin?**

Solution

Attractive forces:

Van der Waals forces – always attractive between particles of the same nature e.g. alumina-alumina -(can sometimes become repulsive between particles of different nature e.g. SiC – Si₃N₄ depending on Hamaker constant of medium see. Slide 7.42). They result from the dipole-dipole interactions. There are three categories –1) permanent- permanent (e.g. hydrogen bonding) –2) permanent- induced dipole, 3) induced dipole –induced dipole – (i.e. instantaneous dipoles from electron cloud fluctuations - London or dispersion forces).

Magnetic interparticle forces between ferromagnetic particles with elements like Fe, Ni, Co and Cr which have permanent magnetic moments.

Forces from oppositely charged particles. Distribution of ions in double layer inverted and thus cancel each other out on approach of the particle surfaces (slide 8.36)

Repulsive forces:

Electrostatic forces coming from particles with surface charges of the same sign. The charged surface induces an electrical double layer when in an electrolyte solution and the overlap of the two double layers as particle approaches gives rise to a repulsive force which depends on surface potential (or charge density).

Steric Forces due to adsorbed polymers (steric stabilization). When the adsorbed layers begin to overlap and interpenetrate there is a repulsion with enthalpic and entropic contributions.

2. **How does the interaction energy between two spherical particles in suspension vary according to the size of a particle and the concentration of ions in solution according to the DLVO theory.**

Solution

The interaction energy is higher when the particle size is larger, that is, more attractive.

The electrostatic repulsive interaction energy is weaker as the ion concentration increases because the double layer is compressed. (see slide week 8 no. 39, and week 9 slide 22)

3. **What are the mechanisms that lead to colloidal stabilization by adsorption of polymers with long molecular chains (steric stabilization)? How important is the solvent-polymer interaction?**

Solution

Adsorbed polymers limit the approach distance between particle surfaces. This prevents the particles from being at short distances where the attractive Van der Waals forces predominate. This is steric stabilization. The repulsive force has two types of contribution:

Enthalpic

-There is a change in enthalpy when the particle chains of two particles interpenetrate (decrease in contact area with the solvent) and enthalpy of mixing – change in polymer chain concentration – inducing a concentration gradient and osmotic pressure resulting in a repulsive force, due to the solvent moving towards areas with high polymer concentrations (surface-surface) from areas of lower polymer concentration (bulk solution).

Entropic

There is also a change in entropy due to the fact that the polymers can adopt fewer configurations than when the particle is isolated. The free energy is therefore greater the entropy decreases, which is unfavorable and thus a repulsion is produced.

The solvent-polymer interaction is very important. If the polymer is not in a good solvent then it will prefer to make a polymer-polymer interface rather than polymer solvent interface and lead to flocculation and not dispersion. If the polymer is in a good solvent then the polymer can extend into the solvent and will result in a steric stabilisation as described above.

4. What type of polymer is polyacrylic acid (PAA)? How can it be used to stabilize a suspension of ceramic powder (e.g. alumina Al_2O_3) and at which pH is it most effective?

Solution

PAA is a polyelectrolyte with dissociable carboxylate groups (the majority are dissociated at $\text{pH} > 6$). To stabilize an alumina suspension it is necessary that the PAA is dissociated if not the water is not a good solvent therefore it is necessary that the pH is ≥ 6 . There is the steric effect related to the thickness of the adsorbed layer and electrostatic effect of negatively charged dissociated carboxylate groups - thus together the effect is known as electro-steric stabilization.

5. Calculate the aggregation number (NA) of a micelle formed by a single hydrocarbon (alkyl) chain surfactant having 10 carbons, assuming that the hydrocarbon forms a sphere with a radius equal to the extended length of the hydrocarbon chain. Do the same calculation for hydrocarbon chains comprising 12 and 16 carbons. Note: the aggregation number is $\text{NA} = \text{volume of a micelle} / \text{volume of a surfactant molecule}$.

Solution

Calculation of the length l of the hydrocarbon chain: use Eq. (1.3.3) :

$$l = 0.15 + 0.127n_c \text{ [nm]}$$

where, $n_c = 10$, and is therefore $l = 0.15 + 1.27 = 1.42 \text{ [nm]}$.

The volume of the corresponding sphere $V_s = 4\pi l^3/3 = 1.99 \text{ [nm}^3\text{]}$

Volume v of an alkyl chain can be calculated using Eq. (1.3.2) :

$$v = 0.027(n_c + n_{\text{Me}}) \text{ [nm}^3\text{]}$$

For this case we have one terminal methyl group (and one ionic group at the other end of the alkyl chain), $n_{Me} = 1$, and $v = 0.027 \times 11 = 0.297 \text{ [nm}^3\text{]}$.

The aggregation number NA is the ratio V_s/v : which gives ,

$$NA = 11.99/0.297 = 40.$$

For $nc = 12$, $NA = 56$ and

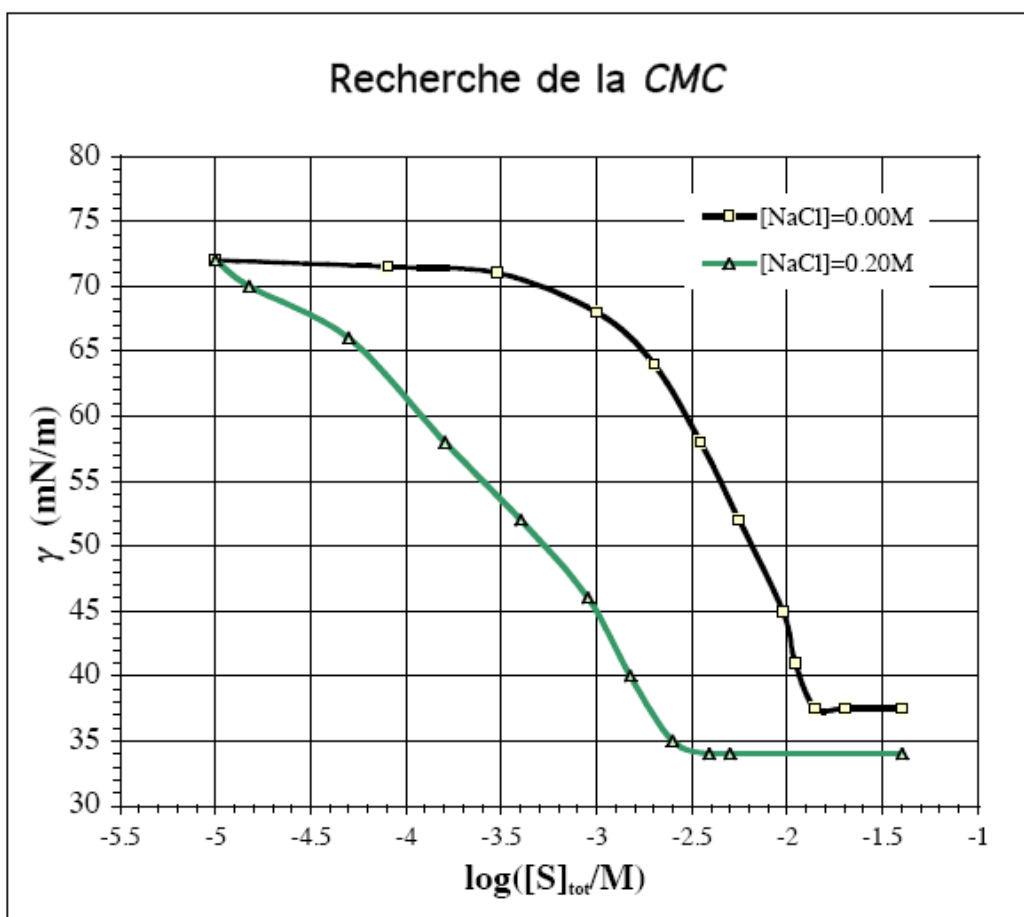
For $nc = 16$, we find $NA = 95$.

6. The figure below shows the change in the surface tension of aqueous solutions as a function of the concentration of dodecylammonium chloride (pure water, or 0.20 [M] aqueous NaCl solution).

i. Explain in molecular terms the influence of surfactant concentration $[S]_{tot}$ on surface tension.

ii. Determine the CMC corresponding to each of the curves.

iii. Explain the influence of NaCl on the CMC.



Solution

- i) As the concentration of surfactant $[S]_{tot}$ increases, an increasing amount of surfactant molecules accumulates at the liquid-vapor interface; the surfactant molecules position themselves at the liquid-vapor interface, exposing their polar heads to the solution, while their alkyl chain is expelled from the solution. The surface tension – interfaccial energy decreases as the concentration increase..up to the...CMC
- ii) To get the CMC we find the break point graphically on each curve (see figure), and read the log value $([S]_{tot} / M) = y$; $CMC = 10^y [M]$.

For $[NaCl] = 0.0 [M]$, we find: $\log [Stot] = -1.9 \Rightarrow [Stot] = 10^{-1.9} = 1.26 \times 10^{-2} [M]$

For $[\text{NaCl}] = 0.20 \text{ [M]}$, we find: $\log [\text{Stot}] = -2.6 \Rightarrow [\text{St}] = 10^{-2.6} = 1.53 \times 10^{-3} \text{ [M]}$

- iii) An increase in the electrolyte concentration has the effect of increasing the ionic strength of the solution, and therefore of decreasing the range of repulsive electrostatic forces between the ionized heads of the surfactant molecules; therefore, the aggregation of the surfactant molecules into micelles is easier and the critical concentration of micelle formation is lowered.

7. Using the Hamaker software - what is the distance of the secondary minimum for a Sumitomo AA04 alumina in the presence of Y^{3+} ions (concentration below). What is the electrostatic barrier necessary for a stability of one day for a suspension (30% by weight) of AA04 doped with Y^{3+} . What is the thickness of the adsorbed layer necessary for steric stabilization?

Data : Al_2O_3 - Hamaker constant: $3.67 \cdot 10^{-20} \text{ J}$, AA04 – Sumitomo - $D_{v10} = 200 \text{ nm}$ $D_{v50} = 500 \text{ nm}$ $D_{v90} = 1655 \text{ nm}$, $\text{pH} = 4$, ζ potential 60 mV (zeta plane = Debye length (double layer thickness). - HNO_3 (0.005M) Dopants Y^{3+} (nitrate salt- 0.005M)

Solution

With Hamaker software and the double layer thickness at the zeta plane

For Y^{3+} and HNO_3^- secondary minimum of -5.99 kT at 17.70 nm ($\kappa^{-1} = 1.84 \text{ nm}$)

The electrostatic barrier for one day stability with Y^{3+} is 23.49 mV

For Y^{3+} - a 20 nm layer is needed - but which always gives a secondary minimum of -2.19 kT at 40nm

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8. Give an example of the use of colloidal chemistry in everyday life.

Ceramic processing, food (milk - emulsion), detergents, paints, cosmetics, cooking