Answers CS Exam Part I (Philipse) April 2021.

1 a) $\dfrac{ze\Psi(\mathrm{midplane})}{kT} \ll 1 \;\Rightarrow \Psi(\mathrm{midplane}) \ll 25\ \mathrm{mV}$ for $z = 1$.

b) A_{rep}: repulsive energy per unit area $(\mathrm{J/m^2})$

LHS and the RHS in (5.60) both have the unit of $\mathrm{m^{-2}}$

c) The EDL-repulsion stems from a net ionic osmotic pressure between charged surfaces, which equals *total* ionic osmotic pressure minus the Maxwell stress. The latter is due to the net electro-static attraction between ions and the surfaces. The only electrostatic repulsion in the system is that between surfaces and *co*-ions, which is overruled by the attraction between counter-ions and surfaces (leading to the negative Maxwell pressure). So the term ‘electrostatic repulsion’ is misleading, if not simply wrong – it probably stems from the mistaken notion that two surfaces with the same charge sign repel, just as two ions, by Coulombic repulsion. Note in this respect that in the Donnan limit of strongly overlapping EDL’s, electrical potentials are constant (no electrostatic forces present) but there still is an EDL-repulsion.

Here the student can show in the argumentation that he understands the essentials of the EDL repulsion; bonus point for the insight that the Donnan limit disproves the notion of an electrostatic EDL repulsion.

d) $\dfrac{A_{\mathrm{tot}}(h)}{kT} = 64\rho_s\kappa^{-1}\tanh^2(\Phi_0/4)\ \exp[-\kappa h] - \dfrac{A}{12\pi kTh^2} \quad (\mathrm{m^{-2}})$

e) $$\frac{A_{\text{tot}}(\kappa h)}{kT} = 64\rho_{\text{s}}\kappa^{-1}\tanh^2(\Phi_0/4)\ e^{-\kappa h} - \frac{\kappa^2 A}{12\pi kT(\kappa h)^2} \quad (\text{m}^{-2})$$

$$= \alpha e^{-\kappa h} - \frac{\beta}{(\kappa h)^2}$$

Flocculation criterion: $\frac{dA_{\text{tot}}}{d(\kappa h)} = 0 \Rightarrow (\kappa h_{\text{max}})^3 \alpha e^{-\kappa h} = 2\beta$ (1)

and $A_{\text{tot}} = 0 \Rightarrow (\kappa h_{\text{max}})^2 \alpha e^{-\kappa h} = \beta$ (2)

Divide (1) by (2) $\Rightarrow \kappa h_{\text{max}} = 2$ (3)

Put (3) into (2) $\Rightarrow \alpha = \frac{e^2}{4}\beta$ (4)

Substitution α and β in (4) $\Rightarrow \frac{\kappa^3}{\rho_{\text{floc}}} = \frac{\text{const}_1}{A}\tanh^2(\Phi_0/4)$ (5)

Put $\kappa^2 \propto \rho_{\text{floc}} z^2$ in (5) $\Rightarrow \rho_{\text{floc}} = \frac{\text{const}_2}{A^2 z^6}\tanh^4(\Phi_0/4)$ (6)

If the surface potential goes up, [salt-floc] goes up, and high-valent ions strongly reduce it.

NB: the method followed here is also applied in Tutorial exercise 5.15 where the flocculation salt concentration is evaluated for an EDL-repulsion in the Debye-Hückel approximation.

f) For high surface potential, the hyperbolic tangent equals one, hence:

$$\rho_{\text{floc}} = \frac{\text{const}_2}{A^2 z^6} \quad , \quad \text{for } \Phi_0 = \frac{ze\Psi_0}{kT} \gg 1 \quad (7)$$

In the Debye-Hückel limit we have (linearize the hyperbolic tangent):

$$\rho_{\text{floc}} = \frac{\text{const}_3}{A^2 z^2}\Psi_0^4 \quad , \quad \text{for } \Phi_0 = \frac{ze\Psi_0}{kT} \ll 1 \quad (8)$$

g) Defence: when the salt concentration is high enough for the plates to (almost) aggregate, the repulsive barrier will be low and the mid-plane potential will be small, so the weak-overlap approximation will be justified, even if plates are close. Or: the WLO is valid when *h* is much larger than the Debye-length; at high salt conc. That is almost always the case