Exercise 1 Debye-Hückel approximation

The Debye-Hückel theory predicts an exponentially decaying profile for ψ with the distance r. The Debye length, k^{-1}, can be calculated from the following equation

$$k^{-1} = \left[\frac{N_A e^2}{\epsilon\epsilon_0 k_B T}\sum_i z_i^2 c_i^\infty\right]^{-1/2} = \left[A(T)\sum_i z_i^2 c_i^\infty\right]^{-1/2},$$

where c_i^∞ is the concentration of ions of type i, expressed in $\mathrm{mol\,m^{-3}}$. In aqueous solvent at 298 K, $A(T) = 5.404 \times 10^{15}\,\mathrm{m/mol}$.

(a) Calculate the Debye lengths in 0.01 mol/l aqueous solutions of NaCl, $CaCl_2$, $AlCl_3$, and $MgSO_4$ at 298 K.

(b) What happens to Debye length when the concentration of electrolyte is increased? For example, try to sort these concentrations of electrolytes: 2:2, 2:1, 1:1, 3:1, 1:2, and 3:2; respect to the Debye length.

Solution to Exercise 1

(a) NaCl

$$\sum_i z_i^2 c_i^\infty = (1^2 + 1^2)\cdot 10^1\,\mathrm{mol\,m^{-3}} = 20\,\mathrm{mol\,m^{-3}}$$

$$k^{-1} = \left[5.404 \times 10^{15}\,\mathrm{m/mol}\cdot 20\,\mathrm{mol\,m^{-3}}\right]^{-1/2} = 3.04 \times 10^{-9}\,\mathrm{m}$$

$CaCl_2$

$$\sum_i z_i^2 c_i^\infty = (2^2 + 2\cdot 1^2)\cdot 10^1\,\mathrm{mol\,m^{-3}} = 60\,\mathrm{mol\,m^{-3}}$$

$$k^{-1} = \left[5.404 \times 10^{15}\,\mathrm{m/mol}\cdot 60\,\mathrm{mol\,m^{-3}}\right]^{-1/2} = 1.76 \times 10^{-9}\,\mathrm{m}$$

$AlCl_3$

$$\sum_i z_i^2 c_i^\infty = (3^2 + 3\cdot 1^2)\cdot 10^1\,\mathrm{mol\,m^{-3}} = 120\,\mathrm{mol\,m^{-3}}$$

$$k^{-1} = \left[5.404 \times 10^{15}\,\mathrm{m/mol}\cdot 120\,\mathrm{mol\,m^{-3}}\right]^{-1/2} = 1.24 \times 10^{-9}\,\mathrm{m}$$

$MgSO_4$

$$\sum_i z_i^2 c_i^\infty = (2^2 + 2^2)\cdot 10^1\,\mathrm{mol\,m^{-3}} = 80\,\mathrm{mol\,m^{-3}}$$

$$k^{-1} = \left[5.404 \times 10^{15}\,\mathrm{m/mol}\cdot 80\,\mathrm{mol\,m^{-3}}\right]^{-1/2} = 1.52 \times 10^{-9}\,\mathrm{m}$$

(b)

$$k^{-1}[1:1] > k^{-1}[1:2] = k^{-1}[2:1] > k^{-1}[2:2] > k^{-1}[3:1] > k^{-1}[3:2]$$

Exercise 2 Beyond Debye-Hückel: Grahame model

The Debye-Hückel approximation of the diffuse part of the electrostatic double layer doesn't hold when the potential is considerate. A complete solution of the Poisson-Boltzmann equation provides a better description of the variation of potential ψ with distance.

The Grahame equation gives the relationship between the interfacial charge density and the potential at the interface. This relation can be derived assuming the overall electroneutrality condition. This condition demands that the total charge, i.e. the surface charge plus the charge of the ions in the whole double layer, must be zero. Since the total charge in the double layer is $\int_0^\infty \rho\, dx$, we have

$$\sigma_S = -\int_0^\infty \rho\, dx, \tag{1}$$

where x is the direction perpendicular to the interface.

(a) How should behave $\psi(x)$ at distances far away from the surface?

(b) Write and simplify σ_S for systems with symmetric electrolytes (i.e. $z_i = z$ and $c_i^\infty = c^\infty$) using the Poisson's equation and the results obtained in the previous point.
Hint: make use of this identity

$$\left[e^{-ax} + e^{ax} - 2\right] = \left[e^{-\frac{ax}{2}} - e^{\frac{ax}{2}}\right]^2$$

(c) Calculate the surface potential at 298 K in 10 mol m^{-3} of NaCl solution (ϵ=78.5), in which the surface charge density is -0.1 C m^{-2}, using the Grahame equation obtained at the previous point.
Hint: The Grahame equation looks like this

$$\sigma_S = (8RT\epsilon\epsilon_0 c^\infty)^{\frac{1}{2}} \sinh\left(\frac{ze\psi_0}{2k_BT}\right),$$

where $\psi_0 \equiv \psi(x=0)$.

Solution to Exercise 2

(a-b) *This is a recap of what we have been doing during the last "interactive" exercise session.*

If we drop the assumption of low potential that leads to Debye–Hückel approximation, the Poisson–Boltzmann equation for a symmetric salt in one dimension (i.e. we assume that electric field doesn't depend on x and y) becomes

$$\frac{d^2y}{dx^2} = \frac{c^\infty e^2}{\epsilon\epsilon_0 k_B T} \cdot (e^{-y} - e^{y}),$$

where $y = e\psi/k_BT$ is the dimensionless potential. We note the identity $\sinh y = 1/2 \cdot (e^{-y} - e^{y})$, and we can solve the differential equation by multiplying both sides by $2 \cdot dy/dx$:

$$2 \cdot \frac{dy}{dx} \cdot \frac{d^2y}{dx^2} = 2 \cdot \frac{dy}{dx} \kappa^2 \sinh y.$$

The left-hand side is the first derivative of $(dy/dx)^2$. We substitute this and integrate:

$$\int \frac{d}{dx'}\left(\frac{dy}{dx'}\right)^2 dx' = 2\kappa^2 \int \frac{dy}{dx'} \sinh y\, dx'$$

$$\left(\frac{dy}{dx}\right)^2 = 2\kappa^2 \int \sinh y'\, dy' = 2\kappa^2 \cosh y + C_1.$$

Cont.

C_1 is an integration constant and it is determined by boundary conditions: at large distances the potential and its derivative must be zero. Since $\cosh y = 1$ for $y = 0$, this constant is equal to $-2\kappa^2$. Thus we have:

$$\left(\frac{dy}{dx}\right)^2 = 2\kappa^2(\cosh y - 1) \Longrightarrow \frac{dy}{dx} = -\kappa\sqrt{2\cosh y - 2}$$

The minus sign in front of the square root comes from the physical fact that a positive potential must decrease with increasing distances. Using the mathematical identity $\sinh y/2 = \sqrt{1/2(\cosh y - 1)}$, we have finally

$$\frac{dy}{dx} = -2\kappa \sinh\frac{y}{2}.$$

Starting from the relation that enforces electroneutrality, we can use the Poisson equation to find the dependence of σ_s on the potential ψ:

$$\sigma_S = -\int_0^\infty \rho \mathtt{d}x = \epsilon\epsilon_0 \int_0^\infty \left(\frac{\mathtt{d}^2\psi}{\mathtt{d}x^2}\right)\mathtt{d}x = \epsilon\epsilon_0\left[\left.\frac{d\psi}{dx}\right|_\infty - \left.\frac{d\psi}{dx}\right|_0\right] = -\epsilon\epsilon_0\left.\frac{d\psi}{dx}\right|_0.$$

With $dy/dx = -2\kappa \sinh y/2$ and

$$\frac{dy}{dx} = \frac{d(e\psi/k_BT)}{dx} = \frac{e}{k_BT}\frac{dy}{dx},$$

we get to the Grahame equation

$$\sigma_s = \sqrt{8c^\infty\epsilon\epsilon_0 k_B T}\sinh\frac{e\psi_0}{2k_BT}$$

(c) Note that if the electrolytes concentration (c^∞) is expressed in $\mathrm{mol\,m^{-3}}$, we have to use the identity $k_B/N_A = R$. Inserting the numbers in Grahame equation:

$$\psi_0 = \left(\frac{2kT}{e}\right)\sinh^{-1}\left[\frac{\sigma_S}{\sqrt{8RT\epsilon\epsilon_0 c^\infty)}}\right] = \frac{2\cdot 1.381\cdot 10^{-23}\cdot 298}{1.602\cdot 10^{-19}}\sinh^{-1}\left(-\frac{0.1}{\sqrt{8\cdot 8.314\cdot 78.5\cdot 8.854\cdot 298\cdot 10^{-12}\cdot 10}}\right) =$$

$$= 0.0514\,\mathrm{V}\times(-2.84) = -146\,\mathrm{mV}.$$

The End.