Physical Chemistry of Interfaces:

Exercises *Session 6*

6.1 Debye length

note: the product $\varepsilon_0\varepsilon_r$ is equal to the permittivity ε defined in the lecture notes.

The Debye Hückel parameter is given by:

$$\kappa = \left(\frac{F^2 \sum_i c_i z_i^2}{\varepsilon_0 \varepsilon_r RT}\right)^{\frac{1}{2}} \qquad [m^{-1}]$$

where F is the Faraday constant, ε_0 is the permittivity of the vacuum, ε_r is dimensionless relative permittivity and c is concentration of the ions in mol m^{-3}.

F=96485 C mol^{-1}, $\varepsilon_0 = 8.8510^{-12}\ \mathrm{C\ V^{-1} m^{-1}}$, $\varepsilon_r = 78.5$, R=8.314 $JK^{-1}mol^{-1}$

Check the units of the variables and find the unit of κ. Calculate the Debey length for the following concentrations of salts in water at 25 ° C:

a) 10^{-2} M KCL
b) 10^{-6} M KCL
c) 10^{-3} M NaCl + 10^{-4}M Na_2SO_4

Solution:

The units:

$$\kappa = \left(\frac{F^2 \sum_i c_i z_i^2}{\varepsilon_0 \varepsilon_r RT}\right)^{\frac{1}{2}} = \left(\frac{\mathrm{C^2 mol^{-2}} \sum_\mathrm{i} \mathrm{mol\ m^{-3}}}{\mathrm{CV^{-1} m^{-1} JK^{-1} mol^{-1} K}}\right)^{\frac{1}{2}} = \left(\frac{\mathrm{C^2 mol^{-2}} \sum_\mathrm{i} \mathrm{mol\ m^{-3}}}{\mathrm{CV^{-1} m^{-1} C\ V\ K^{-1} mol^{-1} K}}\right)^{\frac{1}{2}}$$

$$= \left(\frac{\mathrm{C^2 mol^{-1}\ m^{-3}}}{\mathrm{C^2 m^{-1} mol^{-1}}}\right)^{\frac{1}{2}} = (\mathrm{m^{-2}})^{\frac{1}{2}} = \mathrm{m^{-1}}$$

note: the factor 1000 comes from converting concentrations between molar (M) and moles per cubic meter

I. $\kappa = (\frac{2000F^2}{\varepsilon_0\varepsilon_r RT})^{\frac{1}{2}}\sqrt{I} = 3.2897 * 10^9\sqrt{I}\ (m^{-1}) = 3.2897\sqrt{I}\ (nm^{-1})$

$$I = \frac{1}{2}\big((0.01*1) + (0.01*1)\big) = 0.01\, mol/L$$

$$\kappa = 3.2897\sqrt{I} = 0.329\, nm^{-1}$$

$$\boldsymbol{\kappa^{-1} = 3.04\ \mathrm{nm}}$$

II. $\boldsymbol{\kappa^{-1} = 304\ \mathrm{nm}}$

III. $I = \frac{1}{2}(10^{-3} + 10^{-3} + 2*(1*10^{-4}) + 10^{-4}*2^2) = 13*10^{-4}\, mol/L$

$$\boldsymbol{\kappa^{-1} = 8.44\ \mathrm{nm}}$$

6.2

For an electrophysiological experiment you form an electrode from a 5 cm long platinum wire (0.4 mm diameter) by bending it in the shape of a spiral. Calculate the total capacitance of the diffuse electric double layer for aqueous solutions of a monovalent salt at concentrations of 0.1 and 0.001 M. Assume a low surface potential.

Solution:

From the concentration of solution, we can calculate the Debye length:

$$\lambda_D = \frac{1}{\kappa} = \left(\frac{1000\,F^2\sum_i c_i z_i^2}{\varepsilon_0\varepsilon_r RT}\right)^{-\frac{1}{2}} = \frac{\sqrt{\varepsilon_0\varepsilon_r RT}}{\sqrt{1000}F\sqrt{2c}}$$

$$= \frac{\sqrt{78.5\ \cdot 8.85\cdot 10^{-12}\cdot 8.314\cdot 298.15}}{96485\cdot\sqrt{2000\,c}} = \frac{3.04\cdot 10^{-10}}{\sqrt{c}}$$

$$= \frac{3.04\cdot 10^{-10}}{\sqrt{0.001}} = \mathbf{9.6\ nm}$$

$$\lambda_D = \frac{3.04\cdot 10^{-10}}{\sqrt{0.1}} = \mathbf{0.96\ nm}$$

Capacity per unit area can be then computed using Gouy-Chapman model as

$$C = \frac{\varepsilon_0\varepsilon_r}{\lambda_D} = \frac{78.5\ \cdot 8.85\cdot 10^{-12}}{9.6\ \cdot 10^{-9}} = \mathbf{0.072\ F/m^2}$$

$$C = \frac{\varepsilon_0\varepsilon_r}{\lambda_D} = \frac{78.5\ \cdot 8.85\cdot 10^{-12}}{0.96\ \cdot 10^{-9}} = \mathbf{0.72\ F/m^2}$$

To obtain the total capacities we have to multiply this with the surface area. Neglecting the end cap the surface area is $A=\pi\cdot 0.4\times 10^{-3}$ m $\cdot$ 0.05 m = 6.3×10^{-5} m^2.

The total capacities are **4.5 μF** and **45 μF**, respectively.

6.3 The differential capacitance of a mercury electrode in an aqueous medium containing NaF has been measured at the point of zero charge. It is 6.0 μF/cm2 at 1 mM, 13.1 μF/cm2 at 10 mM, 20.7 μF/cm2 at 100 mM, and 25.7 μF/cm2 at 1 M concentration. Compare this with the result of the Gouy–Chapman theory and draw conclusions.

Solution:
For $\psi 0 = 0$ and considering that cosh 0 = 1, the Gouy-Chapman model reduces into simple form:

$$C = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D}$$

With $\varepsilon = 78.4$ for water we get

$$\lambda_D = \frac{3.04 \cdot 10^{-10}}{\sqrt{0.001}} = 9.61\text{nm}\,,\ C = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} = 7.2\ \mu\text{F/cm}^2$$
$$\lambda_D = \frac{3.04 \cdot 10^{-10}}{\sqrt{0.01}} = 3.04\text{ nm}\,,\ C = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} = 22.9\ \mu\text{F/cm}^2$$
$$\lambda_D = \frac{3.04 \cdot 10^{-10}}{\sqrt{0.1}} = 0.961\text{nm}\,,\ C = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} = 72.3\ \mu\text{F/cm}^2$$
$$\lambda_D = \frac{3.04 \cdot 10^{-10}}{\sqrt{1}} = 0.304\text{ nm}\,,\ C = \frac{\varepsilon_0 \varepsilon_r}{\lambda_D} = 229\ \mu\text{F/cm}^2$$

Compared to the experimental results this clearly shows, that Gouy-Chapman theory fails to describe the capacitance of the double-layer, especially at high salt concentration.

Problem 6.4

solution:

We take two alkyethylene glycols with the same head group but different tail length, namely C_8E_6 and $C_{12}E_6$. Their CMCs are 9.8mM and 0.08mM respectively. The Gibbs energies of micellization can be estimated by:

$$\Delta G = RT \ln c_{\text{cmc}}$$

This yields Gibbs micellization energies of -11.5 kJ/mol and -23.4 kJ/mol, respectively. Division of this difference by 4 yields a value of 3.0 kJ/mol per alkyl link.