

## Physical Chemistry of Interfaces:

### Exercises Session 6

*note: the product  $\epsilon_0\epsilon_r$  is equal to the permittivity  $\epsilon$  defined in the lecture notes.*

#### 6.1 Debye length

The Debye Hückel parameter is given by:

$$\kappa = \left( \frac{F^2 \sum_i c_i z_i^2}{\epsilon_0 \epsilon_r RT} \right)^{\frac{1}{2}} \quad [\text{m}^{-1}]$$

where  $F$  is the Faraday constant,  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon_r$  is dimensionless relative permittivity and  $c$  is concentration of the ions in  $\text{mol m}^{-3}$ .

$$F=96485 \text{ C mol}^{-1}, \epsilon_0 = 8.85 \cdot 10^{-12} \text{ C V}^{-1}\text{m}^{-1}, \epsilon_r = 78.5, R=8.314 \text{ J K}^{-1}\text{mol}^{-1}$$

Check the units of the variables and find the unit of  $\kappa$ . Calculate the Debye length for the following concentrations of salts in water at 25 °C:

- a)  $10^{-2} \text{ M KCl}$
- b)  $10^{-6} \text{ M KCl}$
- c)  $10^{-3} \text{ M NaCl} + 10^{-4} \text{ M Na}_2\text{SO}_4$

#### 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.

**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  $6.0 \mu\text{F}/\text{cm}^2$  at 1 mM,  $13.1 \mu\text{F}/\text{cm}^2$  at 10 mM,  $20.7 \mu\text{F}/\text{cm}^2$  at 100 mM, and  $25.7 \mu\text{F}/\text{cm}^2$  at 1 M concentration. Compare this with the result of the Gouy–Chapman theory and draw conclusions.

**6.4** Micellization is driven by the hydrophobic effect. Estimate from measured CMCs of alkylethylene glycols (e.g. for  $\text{C}_8\text{E}_6$  and  $\text{C}_{12}\text{E}_6$ ; CMCs are 9.8 and 0.08mM, respectively) the change in the Gibbs free energy for bringing one methylene group ( $\sim\text{CH}_2\sim$ ) from an aqueous medium into the interior of a micelle.