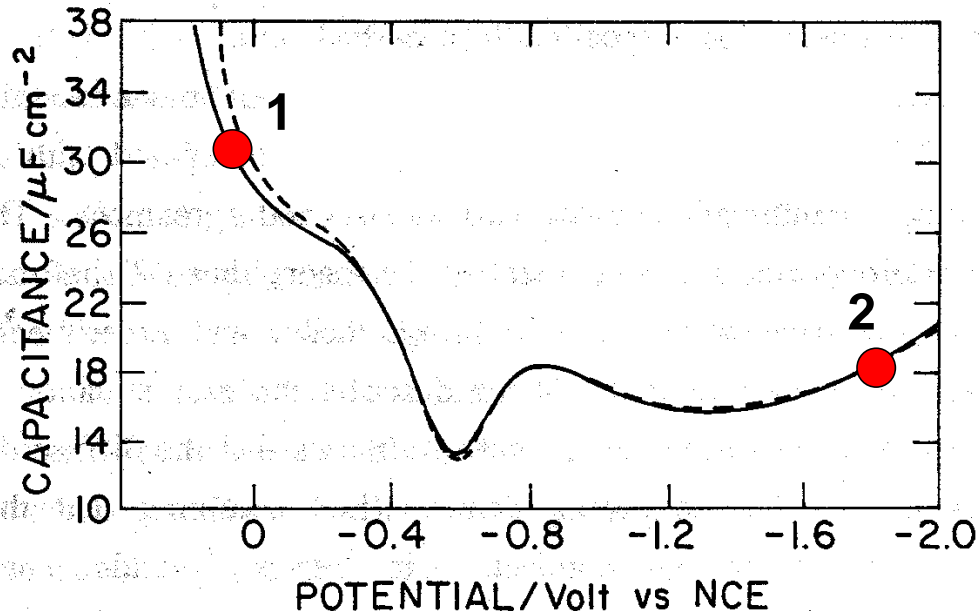


## Exercise Series 3

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1. **Double layer models.** The picture below shows experimental data for the double layer capacity of an electrode in NaF solution (from Grahame, J. Am Chem. Soc. 76, 4819, 1954.).



- Specify the potential of zero charge  $E_{pzc}$  vs. SHE (NCE is the Normal or Standard Calomel Electrode, you can look up its potential vs. SHE in the lecture notes or in any decent electrochemistry textbook). Which metal does  $E_{pzc}$  correspond to? Specify, in which potential region the excess charge on the electrode is positive or negative.
- Identify in the plot the regions, in which the double layer capacity is dominated by the compact layer and by the diffuse layer. In which potential region can you expect to observe specific adsorption?
- Sketch the distribution of ions in the double layer region at the marked points 1 and 2 and draw the corresponding potential distributions (based on the double layer models considered in the lecture). Distinguish Inner Helmholtz Plane, Outer Helmholtz Plane and diffuse layer in your plots.
- Estimate the radius of hydrated ions from the above plot of capacity. Which potential region and which double layer model is most appropriate for his analysis? Use the reduced dielectric constant  $\epsilon_r = 10$  of water at the interface for this calculation.
- Use the Gouy-Chapman model to determine the Debye-length (with  $T = 25^\circ\text{C}$ ,  $\epsilon_r = 10$ ). Finally, calculate the concentration of the electrolyte.

Overall, you see, that if used together, experimental data on double layer capacity, phenomenological understanding of effects in different potential regions, and use of appropriate models can be exploited for diagnostic purposes.

2. If a number of different ionic species with bulk concentrations  $c_i^0$  and valences  $z_i$  are present in solution, the **inverse Debye length** is given by

$$\kappa = \sqrt{\frac{F^2}{\epsilon\epsilon_0 RT} \sum_i c_i^0 z_i^2}.$$

Human blood plasma, that is blood without red and white blood cells and without thrombocytes, contains 143 mM  $\text{Na}^+$ , 5 mM  $\text{K}^+$ , 2.5 mM  $\text{Ca}^{2+}$ , 1 mM  $\text{Mg}^{2+}$ , 103 mM  $\text{Cl}^-$ , 27 mM  $\text{HCO}_3^-$ , 1 mM  $\text{HPO}_4^{2-}$  and 0.5 mM  $\text{SO}_4^{2-}$ . What is the Debye length? Use the dielectric constant  $\epsilon_r = 78$  of water.

3. At the metal|solution interface, a gold electrode with Au(111) surface conformation (lattice constant  $a = 4.08\text{\AA}$ ), is charged with 0.5 negative excess charges per unit cell. The aqueous solution consists of 10 mM NaCl.

- Why can you assume that specific adsorption of ions does not interfere with the formation of an electrical double layer for the conditions provided?
- Use the Gouy-Chapman model (expression provided in the lecture) to calculate the difference between the potential at the interface and the potential in the bulk of the solution, i.e.  $\varphi_{\Delta,0} = \varphi(x=0) - \varphi^s$ . Compare with the corresponding value calculated in the Debye-Hückel approximation.
- Calculate the double layer capacities in Gouy-Chapman model and Debye-Hückel approximation. Discuss the differences.
- To which value would the excess surface charge have to be reduced so that the Debye-Hückel approximation would become applicable?

4. **Supporting electrolyte.** Adsorption of ions from the electrolyte solution is important in studying adsorption phenomena on metal electrodes. Suppose we want to study specific adsorption of an anionic species  $\text{A}^-$ . The concentration of the salt AB in the bulk of the solution is 0.01 M. In addition to that, there is a supporting electrolyte CD of concentration 5M. The surface charge of the metal electrode is  $\sigma^M = 0.3 \text{ C/m}^2$ . We will use the Gouy-Chapman theory to study the role of the supporting electrolyte. Unfortunately, this theory can only be used directly for a situation with only one (z-z) electrolyte. Therefore, we have to proceed in several steps.

- Consider the situation when the supporting electrolyte is absent. Calculate the surface potential  $\varphi_{\Delta,0}$ . Calculate the concentration of  $\text{A}^-$  at the surface. What is the ratio between surface concentration and bulk concentration?
- Now consider the situation when only the supporting electrolyte is present. Perform the same calculation as in a). What is the surface potential  $\varphi_{\Delta,0}$  in this case?
- What is the effect of the potential distribution calculated for the situation in b) on the distribution of  $\text{A}^-$ ? Discuss how the supporting electrolyte works.