

Lecture V

Debye length

The Debye length λ_D can be calculated from the following equation:

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

where:

N_A Avogadro number [6,022 10²³ (mol⁻¹)]

e charge of an electron [1,6 10⁻¹⁹ (C)]

ϵ_0 permittivity of free space [8,85 10⁻¹² (F/m)]

ϵ dielectric constant (water ~80)

kT thermal energy

→ Boltzman constant x absolute T (in K) [k= 1,38 10⁻²³ J/K]

z_i valence number of the specie i

c_i^∞ is the concentration of the ion i expressed in mol/m³.

In aqueous medium at 298K we have that

$$\frac{N_A e^2}{\epsilon \epsilon_0 k T} = 5.404 \cdot 10^{15} \text{ m/mol}$$

Therefore we can calculate the Debye length as

$$\lambda_D = \left(5.404 \cdot 10^{15} \sum_i z_i^2 c_i^\infty \right)^{-1/2} \quad \text{at 298 K}$$

PROBLEM 1

Calculate the Debye lengths in 10mol/m³ aqueous solutions of NaCl, CaCl₂ and AlCl₃ at 298K.

Solution

For NaCl:

$$\sum_i z_i^2 c_i^\infty = (1)^2 \cdot 10 + (1)^2 \cdot 10 = 20 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 20)^{-1/2} = 3.04 \cdot 10^{-9} \text{ m}$$

For CaCl₂:

$$\sum_i z_i^2 c_i^\infty = (2)^2 \cdot 10 + (1)^2 \cdot 2 \cdot 10 = 60 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 60)^{-1/2} = 1.76 \cdot 10^{-9} \text{ m}$$

For AlCl₃:

$$\sum_i z_i^2 c_i^\infty = (3)^2 \cdot 10 + (1)^2 \cdot 3 \cdot 10 = 120 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 120)^{-1/2} = 1.24 \cdot 10^{-9} \text{ m}$$

$$1 \text{ l} = 1 \text{ dm}^3$$

$$1 \text{ (mol/dm}^3\text{)} = 1000 \text{ (mol/m}^3\text{)} = \\ = 1 \text{ (mmol/l)} = 1 \text{ (mM)}$$

PROBLEM 2

Calculate the Debye length in 1M aqueous solutions of:

- a) NaCl
- b) MgCl_2
- c) MgSO_4

and for

- d) 100mM KCl
- e) 25mM KCl

Solution

a) For NaCl:

$$\sum_i z_i^2 c_i^\infty = (1)^2 \cdot 1000 + (1)^2 \cdot 1000 = 2000 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 2000)^{-1/2} = 3.04 \cdot 10^{-10} \text{ m} = 0.304 \text{ nm}$$

b) For MgCl_2 :

$$\sum_i z_i^2 c_i^\infty = (2)^2 \cdot 1000 + 2 \cdot (1)^2 \cdot 1000 = 6000 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 6000)^{-1/2} = 0.18 \text{ nm}$$

c) For MgSO_4 :

$$\sum_i z_i^2 c_i^\infty = (2)^2 \cdot 1000 + (2)^2 \cdot 1000 = 8000 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 8000)^{-1/2} = 0.15 \text{ nm}$$

d) For KCl 100mM:

$$\sum_i z_i^2 c_i^\infty = (1)^2 \cdot 100 + (1)^2 \cdot 100 = 200 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 200)^{-1/2} = 0.962 \text{ nm}$$

e) For KCl 25mM:

$$\sum_i z_i^2 c_i^\infty = (1)^2 \cdot 25 + (1)^2 \cdot 25 = 50 \text{ mol/m}^3$$
$$\lambda_D = (5.404 \cdot 10^{15} \cdot 50)^{-1/2} = 1.92 \text{ nm}$$

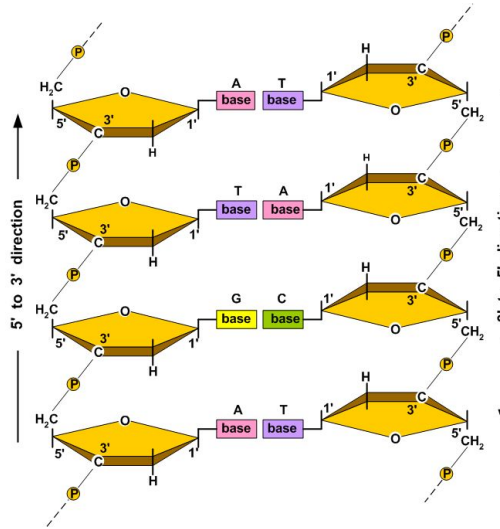
The equivalent capacitance of a DNA layer

PROBLEM 3

1. Calculate the equivalent capacitance of a DNA layer. Explain the approximations made and list the references used.
2. Explain how you could improve the estimation of the equivalent capacitance.

Electrode functionalization:

The sensing surface is fabricated using molecular self-assembly techniques to covalently tether alkanethiol derivatives of single-stranded DNA oligonucleotides to a gold substrate (electrode with 4mm diameter). The formed layer consists of 30-base thiol-modified oligonucleotide probes (5'-pGATCATCTAGCCGGACCCGGGCATCGTGG-3') with $(\text{CH}_2)_6\text{SH}$ at the 3' position. Single stranded DNAs of comparable length are used for the hybridization. We consider the B-DNA structure, which is the most common DNA structure in solution.



The diameter of the DNA helix is 2 nm and the vertical rise per base pair is 0.34 nm (Van Holde 1989). And the tilt of the bases for a B-DNA is 1deg.

Consider that ϵ_0 is the vacuum dielectric constant ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$), and the dielectric constant for DNA, with hybridization ϵ can be approximated to 2.5 (Peterlinz and Georgiadis, 1997 and Yang et al., 1997).

Solution

The formula used to estimate the equivalent capacitance of DNA is

$$C_{dl} = \epsilon_{DNA} \cdot \epsilon_0 \frac{A}{d}$$

where ϵ_0 is the vacuum dielectric constant ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$), for dielectric constant, with hybridization ϵ is equal to 2.5.

The electrode area is $A = 0.1256 \text{ cm}^2$. We can approximately estimate the distance d as:

$$d = (0.34 \cdot 30) \cdot \cos 1^\circ = 10.14 \text{ nm}$$

The final estimation for the equivalent capacitance is

$$C_{dl} = \epsilon_{DNA} \cdot \epsilon_0 \frac{A}{d} = 2.5 \cdot 8.85 \cdot 10^{-12} \text{ F/m} \frac{0.1256 \cdot 10^{-4} \text{ m}^2}{10.14 \cdot 10^{-9} \text{ m}} = 2.74 \cdot 10^{-8} \text{ F} = 27.4 \text{ nF}$$

The values at a certain frequency of the reactive and resistive components of a CPE

PROBLEM 4

Estimate the reactive and resistive components of a CPE for a bare gold electrode, a probe electrode and hybridized one for a frequency of 1kHz.

Consider the following experimental results:

	BARE	PROBE	TARGET
α	0.775	0.867	0.885

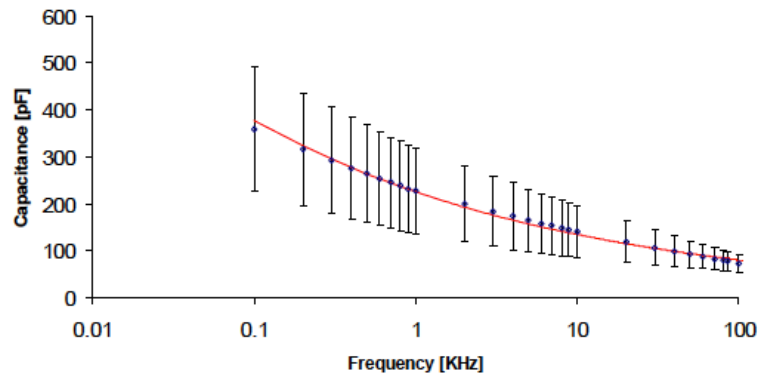


Fig. 2. Average capacitance vs. frequency for the bare electrodes. The bars represent the standard deviation calculated on 30 different biochip sensing areas.

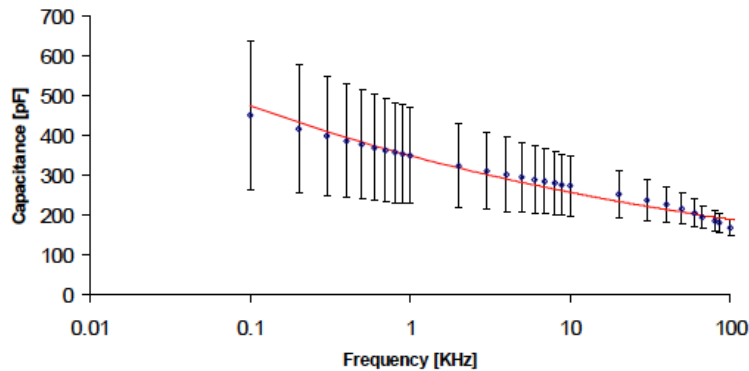


Fig. 3. Average capacitance vs. frequency for the DNA probes immobilized on the gold electrodes. The bars represent the standard deviation calculated on 30 different biochip areas.

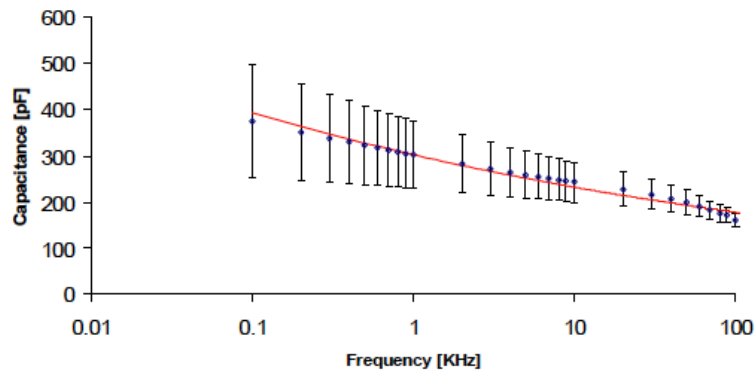


Fig. 4. Average capacitance vs. frequency for the DNA target hybridized with the probes. The bars represent the standard deviation calculated on 30 different biochip areas.

Solution

We can use the formula:

$$Z_{CPE} = \frac{1}{C_p (j\omega)^\alpha} \cong \frac{1}{\omega^\alpha C_p} \sqrt{1-\alpha^2} - j \frac{1}{\omega^\alpha C_p} \alpha$$

where the RESISTANCE components and the REACTANCE components are

$$R_{CPE} \cong \frac{1}{\omega^\alpha C_p} \sqrt{1-\alpha^2}$$
$$X_{CPE} \cong \frac{\alpha}{\omega^\alpha C_p}$$

respectively. From the plots in Fig. 4 we estimate the Capacitance C_{CPE} @1kHz and we calculate the C_p for each electrode, with the formula:

$$C_{CPE} \cong \frac{C_p}{\alpha \cdot \omega^{1-\alpha}}$$
$$C_p = C_{CPE} \cdot \alpha \cdot \omega^{1-\alpha}$$

$$\omega = 2 \pi f$$

You get C_{cpe} graphically at 1 kHz. Then you compute C_p , R_{cpe} and X_{cpe} .

Bare electrodes

$C_p=1.39$ nF

$R_{cpe}= 0.52$ MOhm

$X_{cpe}=0.64$ MOhm

DNA probe

$C_p=1.00$ nF

$R_{cpe}= 0.25$ MOhm

$X_{cpe}=0.43$ MOhm

DNA probe

$C_p=0.79$ nF

$R_{cpe}= 0.26$ MOhm

$X_{cpe}=0.49$ MOhm