1. The Debye parameter (κ) is a very important parameter that helps to describe the structure of the electrical double layer. It is important to know that $\kappa \sim I^{1/2}$. I is the ionic strength ($I = \frac{1}{2}\sum c_i * z_i^2$) that plays a central role in the Debye–Hückel theory as well as in the description of electrokinetic phenomena in colloids and other heterogeneous systems.
   a) Determine the Ionic strength (don't forget to write the units of ionic strength) and the Debye length in water at room temperature (25°C) as a function of the concentration for a solution of NaCl, $CaCl_2$ and $MgSO_4$. (Relative permittivity of water ε_R=78.4).
   b) For the case of NaCl at 0.1mM, compare the Debye length of an aqueous solution with the case of an ethanolic solution (ε_R=24.3).

Solution:

a) The difference among these salts is the valency of the ions.

$$NaCl \rightarrow Na^+ + Cl^-$$
$$CaCl_2 \rightarrow Ca^{+2} + 2Cl^-$$
$$MgSO_4 \rightarrow Mg^{+2} + SO4^{-2}$$

According to the formula, the ionic strength of each salt solution as a function of its concentration is:

1/2[NaCl] + 1/2[NaCl] = [NaCl]
1/2 $[CaCl_2]$*4 +1/2*2$[CaCl_2]$ =3$[CaCl_2]$
1/2 $[MgSO_4]$ *4 + 1/2 $[MgSO_4]$ *4 = 4$[MgSO_4]$

The units of ionic strength are the same as the ones used for the concentration (typically M= mol/L).

We can represent the Debye length as a function of the ionic strength:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{\sum e^2 c_{0i} z_i^2}} = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{2e^2 I}}$$

Where c_{0i} is the concentration far from any surface (in bulk). Notice that it was calculated initially in molarity so we need to multiply it by (N_A*10^3) to have it in atoms/m^3.

Substituting in the equation T=25°C (298K), $\varepsilon_r\varepsilon_0$=8.85*$10^{-12}$*78.4 F/m, N_A=6.022*10^{23}, e=1.60217657*10^{-19} C, k=1.3806488*10^{-23} m^2 kg s^{-2} K^{-1}.

$$\kappa_{NaCl}^{-1} = \frac{0.304}{\sqrt{[NaCl]}}$$
$$\kappa_{CaCl_2}^{-1} = \frac{0.176}{\sqrt{[CaCl_2]}}$$
$$\kappa_{MgSO_4}^{-1} = \frac{0.152}{\sqrt{[MgSO_4]}}$$

Here, the unit of the Debye length is [nm] when the concentration is in [M]

It is important to realize from this problem that:

- The Ionic strength and the Debye length don't depend on the colloids that we have in the solution or how much they are charged, but will depend on the concentration of ions that are in solution.
- The Debye length decreases strongly when we use divalent ions.
- For concentrations of 1M, the Debye length is really short, in the order of 1-3 angstroms that correspond to 1 to 2 atoms. For lower concentrations such as 0.1mM the Debye length could be around the size of a nanoparticle (15-30nm).

b)

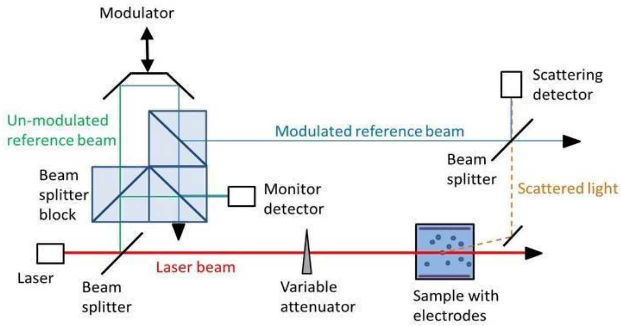
$$\sqrt{\frac{(24.3 * 8.85 * 10^{-12} * 298 * 1.3806488 * 10^{-23}}{(1.60217657 * 10^{-19})^2 * 2 * 0.0001 * 6.022 * 10^{23} * 10^3}} = 16.9 * 10^{-9} m$$

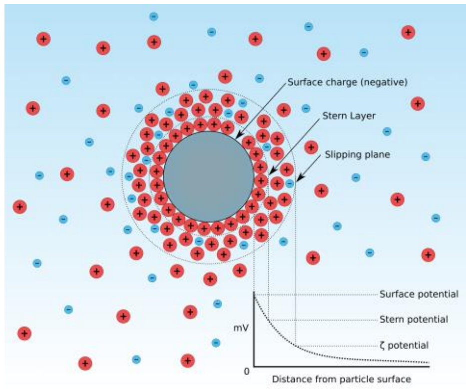
For water: κ_{water}^{-1}= 30.4 nm
For ethanol: $\kappa_{ethanol}^{-1}$= 16. 9 nm

In organic solvents (lower ε_r) the Debye length is shorter. However, realistically salts normally don't dissolve or dissociate very well in organic solvents getting much bigger Debye lengths.

2. One of the ways to characterize the charges on nanoparticles and their interactions with an electrolyte solution is with the use of a Zeta Potential instrument. This instrument is based on the electrophoretic mobility, i.e. the particle solution is placed on an alternating electric field and their mobility (speed/electric field) can be measured illuminating the sample with a laser and analyzing the outgoing beam (either by a Doppler or by a phase analysis). The zeta potential (Potential at the slipping plane) can be calculated using Henry's equation:

$$\mu_E = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta}$$





where ζ is the zeta potential η is the viscosity (1mPa·s for water), a is the radius of nanoparticles, and f(κa) is a Henry's coefficient that is taken as 1.5 for κa >>1 and 1 for κa <<1 (Smoluchowsky's and Huckel's approximations respectively).

a) For 10 mM NaCl solution and 20 nm diameter nanoparticles, calculate the Debye length.

b) What do you think would happen to the zeta potential if we increase the salt concentration? What would happen if we substitute the salt by one with divalent ions?

c) Given a zeta potential of 20 mV at 25° C calculate the electrophoretic mobility using the conditions in a).

d) If the slipping layer were at the stern layer, what would be the total density of charges on the nanoparticle (including the density at the surface plus the density at the stern layer)?

Solution:

a) As seen in one of the former problems:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{\sum e^2 c_{0i} z_i^2}} = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{2e^2 I}}$$

For 10 mM NaCl solution

$$\kappa_{NaCl}^{-1} = \frac{0.304}{\sqrt{[NaCl]}} = 3.04\ nm$$

b) The Debye length decreases, which means that the potential will decrease much faster. Therefore the potential at the slipping plane (Zeta potential) will decrease. The same thing will happen if we increase the valency of the ions.

c) In this case κa = 10/3.04 >>1, so we use the Smoluchowsky's approximation with f(κa)=1.5. ε is the permittivity of water $\varepsilon = 8.85 * 10^{-12} * 78.4\ F/m$

$$\mu_E = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta} = 1.39 \times 10^{-8} m^2/sV$$

d) The diffuse layer can be seen as a capacitor with separation the Debye length. In addition κa >>1 so we can approach this as a parallel-plate capacitor. Then the capacitance per unit area would be.

$$K = \frac{\frac{Q}{A}}{\Delta V} = \frac{\frac{Q_0 + Q_1}{A}}{\Delta V} = \frac{\sigma_0 + \sigma_1}{\Delta V} = \frac{\varepsilon}{\kappa^{-1}}$$

Leading to a surface charge of

$$\sigma_0 + \sigma_1 = \Delta V \varepsilon \kappa = 0.00456\ C/m^2$$