Electrophoresis

Electrophoresis refers to the migration of small charged particles in an electric field. It is frequently used in biology to separate charged particles. A classic example of this is DNA (gel) electrophoresis, where DNA strands are pulled in an electric field through a gel. Based on the length of the DNA strands, they will travel farther in the gel. Comparing the patterns of two electrophoresis experiments on different DNA samples can provide a very powerful test of whether the two samples of DNA fragments are the same. (Frequently the fragments are obtained by mixing proteins which cut the DNA into a solution of long DNA strands. Depending on the base pair sequence on the DNA, the molecule will get cut at different places, and so different sequences lead to different combinations of lengths of DNA strands.)

Let us begin by studying the electrophoresis of small charged particles, such as a small charged ion of sodium in water. Suppose that the charge of the sodium atom is Q, it can be modeled as a sphere of radius R, and it is placed in water, a viscous fluid of viscosity η. Note that, since we are clearly on microscopic scales for this problem, the Reynolds number is always incredbly small, so you may approximate all flows as being in this limit.

(a) Show that if we place this ion in an electric field $\mathbf{E}$, that it will saturate to a steady-state trajectory, traveling at velocity

$$\mathbf{v} = \mu \mathbf{E}.$$

Here μ is called the **mobility**. Find an expression for the mobility in terms of η, Q and R.

(b) Using the fact that $\eta \approx 10^{-3}$ kg/m · s, $R \approx 10^{-10}$ m, and $Q = 1.6 \times 10^{-19}$ C, determine μ. A reasonable electric field in the lab is about 10 V/m – how fast will the ion move?

This result is not quite right, but it is the right order of magnitude. Unfortunately, many objects of interest in electrophoretic studies are quite a bit larger. When we place large charged objects in water, or any other ionic solution, we have to worry about the separation of positive and negative charges in the fluid itself. So let us briefly discuss the electromagnetism of an ionic solution. Suppose that we have a solution of ions of charge $\pm q$, each at density n_0, with the solution at temperature T. It is reasonable to expect that the density of ions is proportional to the Boltzmann weight at temperature T. Suppose that we normalize the electric potential φ so that there is an equal density of positive and negative ions when $\varphi = 0$.

(c) Placing a system at $\varphi \neq 0$ results in an imbalance of positive and negative ions. Show that Poisson's equation should be modified to

$$\nabla^2 \varphi = -\frac{\rho(\varphi)}{\epsilon} = \frac{1}{\lambda^2}\varphi$$

for small φ. Determine the constant λ in terms of n_0, q, T and ϵ.

(d) Suppose that we have a charge Q distributed uniformly on the surface of a sphere of radius R. What is the potential φ which solves the equation of part (c)? (Note that the boundary conditions due to a surface charge are unchanged.). Show that the charge is completely shielded by a sphere of ions with charge $-Q$.

(e) For a typical salty solution relevant for electrophoresis, we have $q = 1.6 \times 10^{-19}$ C, $T \approx 4 \times 10^{-21}$ J, $\epsilon \approx 10^{-11}$ F/m, and $n_0 \sim 10^{26}$ m^{-3}. Determine the value of λ.

(f) Compare the value of λ to the size of the sodium ion. Also compare λ to the size of a large protein (about 10 nm in width). Is λ comparable to the microscopic length scales associated with macromolecules?

(g) Using the formula from part (d), argue that it is probably not very important to account for the salty solution in our formula for μ, so long as $R \ll \lambda$.

Now, let us discuss how electrophoresis through a salty solution is altered when $R \gg \lambda$. It will help to move to a reference frame that moves at velocity $\mathbf{v}_0$ with the charged sphere. In this reference frame, the asymptotic velocity is $-\mathbf{v}_0$. There is one more subtlety: we need to split up the electric potential into $\varphi_{\text{ext}} + \varphi_{\text{int}}$, where φ_{int} is due to the Debye shielding, and φ_{ext} is related to the external field, in the absence of ions. The reason for this is that we know that physically, the application of the electric field will likely not completely ionize the water, but instead simply induce current flow. We now approximate that

$$\nabla^2 \varphi_{\text{int}} = \frac{1}{\lambda^2}\varphi_{\text{int}},$$

i.e. only part of the electric field is effectively contributing to the ionization of the water near the sphere. φ_{ext} on the other hand, simply obey's Laplace's equation.

(h) Using Ohm's Law for electric current on $\mathbf{E}_{\text{ext}}$, translate the assumption that no charge flows into the sphere as a constraint on $\mathbf{E}_{\text{ext}}(\mathbf{x})$ at the boundary of the sphere. Conclude by finding a solution of Laplace's equation φ_{ext} with the appropriate boundary conditions.

(i) Derive the following equation for the fluid velocity, based on balance of forces in the fluid:

$$\nabla P = -\frac{\epsilon}{\lambda^2}\varphi_{\text{int}}\left(\mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{int}}\right) + \eta \nabla^2 \mathbf{v}.$$

(j) Argue that, except for very close to the sphere, we can approximate $\mathbf{E} \approx \mathbf{E}_{\text{ext}}$. Split up the fluid velocity as follows:

$$\mathbf{v} = -\frac{\mathbf{E}_{\text{ext}}}{\mu} + \mathbf{v}',$$

where right now the value of μ is a mystery (we will determine it later). Show that if we make the ansatz

$$\mathbf{v}' = C\varphi_{\text{int}}\mathbf{E}_{\text{ext}}$$

for an appropriate choice of C which you should determine, that so long as $R \gg \lambda$, to leading order in λ, $\mathbf{v}$ will solve the equation of motion from part (i), with $P = 0$.

(k) By imposing physical boundary conditions on $\mathbf{v}$ at the surface of the sphere, conclude that

$$\mu \approx \frac{Q\lambda}{4\pi\eta R^2}.$$

Compare with the result from part (a).

(l) For a protein of charge $Q = 10q$ and $R \sim 10$ nm, estimate the value of μ, and compare with the result of part (b).