Conductivity of an Acid

In this problem, we will explore the conductivity of an electrolytic solution, culminating in the rather curious behavior of the conductivity of an acidic (or, by very similar arguments, basic) solution. Let us begin by considering an electrolytic solution in water, where there is a concentration c_- of anions, each of which carries charge $-Ze$, and a concentration c_+ of hydrogen ions (protons), of charge $+e$. Note that the electric charge $e \approx 10^{-19}$ C.

(a) To avoid huge Coulomb electrostatic energy densities in the water, the charge density must be zero (on macroscopic length scales). Use this to relate c_- to c_+.

From now on in this problem, we will simply denote $c_- = c$.

Now, we know from fluid mechanics that a small object, such as an anion, moving in water experiences viscous drag forces: $\mathbf{F} = -b_\pm \mathbf{v}$, where $b_\pm > 0$, and b_+ corresponds to the coefficient for the proton, and b_- the coefficient for the anion. These charged particles will also experience forces due to externally applied electric fields. Suppose that we apply an external electric field $\mathbf{E}$ to the fluid.

(b) Assuming that all of the ions in the fluid experience no net forces,[1] calculate the velocities of both the protons and the anions.

(c) Show that Ohm's Law holds for this electrolytic solution, and calculate the conductivity σ, as a function of Z, $b_\pm$, e, c and any fundamental constants.

(d) We are considering an acidic solution, so the proton is very light and small compared to the anion. Argue using basic fluid mechanics that the proton contribution to σ is by far dominant. Then, using the fact that the viscosity of water $\eta \approx 10^{-3}\text{Pa} \cdot \text{s}$, and that the effective radius of a proton in water is about 10^{-10} m, estimate the conductivity of water (which can be thought of as an "acid" with $c \approx 10^{20}$ m^{-3}), and compare to the experimental value: $\sigma \approx 5 \times 10^{-6}$ $(\Omega \cdot \text{m})^{-1}$. How much larger would the conductivity of a 0.01 M acid solution be, assuming that the acid has completely dissociated?[2]

In part (c), we determined the answer for the conductivity of an acid, up to the density c of anions. Interestingly, however, c may be quite different from n, the number density of acid molecules. The reason for this is that not all of the acid is in anion form – some of it has protons attached to it. In particular, there is some chemical equilibrium (neglect any intermediate stages, for simplicity):

$$\mathrm{AH}_Z \underset{\beta}{\overset{\alpha}{\rightleftharpoons}} \mathrm{A}^{-Z} + Z\,\mathrm{H}^+.$$

(e) Assume that the acid is in chemical equilibrium, and let $\lambda = c/n$ be the fraction of disassociated acid. Find an equation relating λ and n. Express your answer in terms of the parameter K, defined as

$$\frac{\alpha}{\beta} \equiv (ZK)^Z.$$

(f) Qualitatively sketch σ vs. n, and comment on the resulting behavior.

[1]After we turn on the electric field, there will be some short transient time during which the ions will be experience net forces and therefore acceleration. However, this time is a *microscopic* (and thus very fast) time scale.

[2]Recall the heuristic 1 M $\approx$ 1 nm^{-3}!.