

## Increased Dissociation of Water due to Large Electric Fields

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The first experimental evidence of increased dissociation of weak electrolytes in the presence of large electric fields was reported by Max Wien. Wien observed an increase in the conductivity of a weak electrolyte solution that increased with the strength of the applied electric field.<sup>1,2</sup> Lars Onsager developed the theory behind the effect by using statistical mechanics to determine the rate at which the two dissociated ions diffuse apart as a function of the applied electric field.<sup>3</sup> To obtain an analytical solution to the governing equations, Onsager approximated the ions as having zero size. Experimental and modeling results show that the dissociation of water occurs at a length of  $\sim 0.6$  nm.<sup>4,5,6</sup> In this work, the governing equations proposed by Onsager are solved numerically for weak electrolyte dissociation that occurs at a length of 0.6 nm. The solution obtained is in much better agreement with data for water dissociation in bipolar membranes.

Modeling results show that the dissociation of water takes place via the shifting of electrons along a wire of hydrogen bonds.<sup>6</sup> The modeling results can be simplified to the five steps shown in Figure 1. These steps show randomly oriented water molecules, a hydrogen bonded chain of water molecules, charge separation, the breaking of the hydrogen bonds, and diffusion of the independent charges.

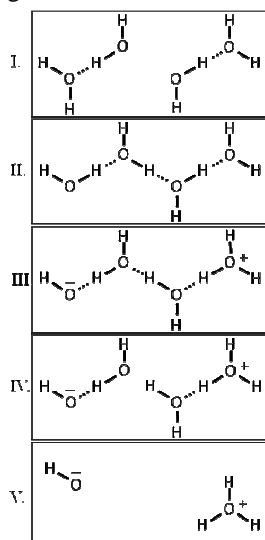


Figure 1. The dissociation of water in five steps.

The problem of interest is to determine the degree of dissociation of pure water as a function of the applied electric field. When the field is applied, the system is not at a thermodynamic equilibrium. However, the system reaches a steady state where the rate of recombination matches the rate of dissociation. At this steady state, the first four steps in Figure 1 are considered equilibrated, and the last step is assumed to follow the Nernst-Planck equation.

The mathematical problem is to solve for the distribution function of ions. The movement of the ions is assumed to follow the Nernst-Planck diffusion equation. There are three parts to the boundary conditions. First, as the ions become infinitely far apart, the distribution function is taken to be an unknown constant. The unknown constant is a measure of the degree of

dissociation. Second, the distribution function is assumed to follow a Boltzmann distribution on a spherical surface at a radius of 0.6 nm. The Boltzmann distribution is a result of the equilibration of the first four steps in Figure 1. Third, the integral of the flux of ions over the surface of the sphere with radius 0.6 nm is zero. Setting the integral to zero specifies the system at steady state. The problem is axisymmetric and can be transformed from a PDE into two ODEs by separation of variables. The ODEs are then solved numerically.

The streamlines of the ions flowing past the central ion when a large electric field has been applied is shown in Figure 2. These streamlines show that the ions are attracted to the central ion. The streamlines are not symmetric. It is this lack of symmetry that leads to the increase in the degree of dissociation.

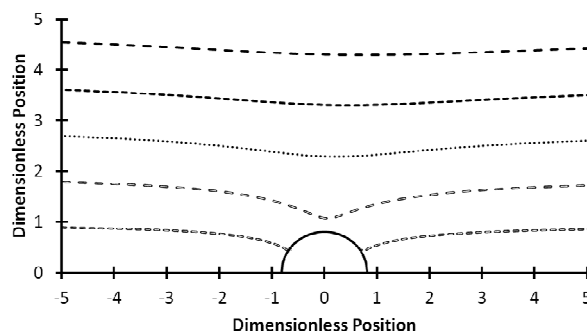


Figure 2. The streamlines of the ions moving in the electric field near the central ion. The solid line is the sphere of radius 0.6 nm.

The degree of dissociation for large electric fields is seen to deviate from the solution using ions of zero size. The logarithm of the ratio of the dissociation constant to the dissociation constant at zero applied field is plotted as a function of field strength in Figure 3. The result with the 0.6 nm sphere increases exponentially.

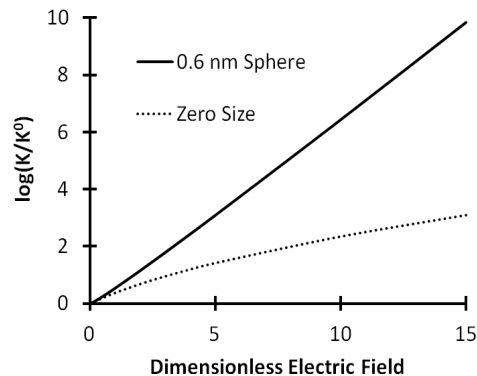


Figure 3. The predicted increase in the dissociation constant as a function of applied electric field.

The solution is of interest in investigations of water in the presence of large electric fields. One application is in the breakdown behavior of bipolar membranes. Other applications include dielectric breakdown and electrode interface phenomena.

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