Activity and activity coefficients II: the logic of the Debye-Hückel equation

In Part I of this series, we concluded that we needed some proportionality factor to relate the activity of a solute (where that activity is not evident to us) to the concentration of that solute (which we can measure directly). That proportionality factor is the activity coefficient γ, so that

$$a_i = (\gamma_i)(m_i)$$

This page considers three key thoughts that must be involved in estimating the activity coefficient γ, and it relates those thoughts to the simplest way we estimate γ, which is through the Debye-Hückel equation. Thus this page attempts to present an intuitive understanding of the Debye-Hückel equation.

Thought #1: the more ions in the solution, the smaller should be the activity coefficient, because those ions can complex with the ion of interest and thus thus render it inactive.

Thought #2: the greater the charge on the ions in solution, the smaller should be the activity coefficient, because greater charge on those ions make them more likely to form a complex with the ion of interest and thus thus render it inactive.

Ionic strength (I) combines both of these by summing the products of concentration and square of the charge for each ion in the solution:

$$I = \frac{1}{2} \Sigma m_i z_i^2$$

Part III of this series considers ionic strength in greater detail.

Thought #3: the greater the charge on the ion of interest, the smaller should be the activity coefficient, because greater charge on that ion makes it more likely to form a complex with other ions and thus be inactive.

The Debye-Hückel expression amplifies this thought by squaring the charge of the ion of interest:

$$\ln (\gamma_i) = - A z_i^2 \sqrt{I}$$

The Debye-Hückel equation was derived by Peter Debye and Erich Hückel in 1925 in a paper in *Physicalische Zeitschrift* (v. 24, p. 185-206).

This mathematical expression yields the expected relationship: the activity coefficient γ decreases with increases in the charge of the ion of interest and/or increase of ionic strength of the solution.