10.4: The Debye-Hückel Theory

The theory of Peter Debye and Erich Hückel (1923) provides theoretical expressions for single-ion activity coefficients and mean ionic activity coefficients in electrolyte solutions. The expressions in one form or another are very useful for extrapolation of quantities that include mean ionic activity coefficients to low solute molality or infinite dilution.

The only interactions the theory considers are the electrostatic interactions between ions. These interactions are much stronger than those between uncharged molecules, and they die off more slowly with distance. If the positions of ions in an electrolyte solution were completely random, the net effect of electrostatic ion–ion interactions would be zero, because each cation–cation or anion–anion repulsion would be balanced by a cation–anion attraction. The positions are not random, however: each cation has a surplus of anions in its immediate environment, and each anion has a surplus of neighboring cations. Each ion therefore has a net attractive interaction with the surrounding ion atmosphere. The result for a cation species at low electrolyte molality is a decrease of μ_+ compared to the cation at same molality in the absence of ion–ion interactions, meaning that the single-ion activity coefficient γ_+ becomes less than 1 as the electrolyte molality is increased beyond the ideal-dilute range. Similarly, γ_- also becomes less than 1.

According to the Debye–Hückel theory, the single-ion activity coefficient γ_i of ion i in a solution of one or more electrolytes is given by

$$\ln \gamma_i = -\frac{A_{\mathrm{DH}} z_i^2 \sqrt{I_m}}{1 + B_{\mathrm{DH}} a \sqrt{I_m}} \tag{10.4.1}$$

where

- The definitions of the quantities A_{DH} and B_{DH} appearing in Eq. 10.4.1 are

$$A_{\mathrm{DH}} \stackrel{\mathrm{def}}{=} \left(N_{\mathrm{A}}^2 e^3/8\pi\right)\left(2\rho_{\mathrm{A}}^*\right)^{1/2}(\epsilon_{\mathrm{r}}\epsilon_0 RT)^{-3/2} \tag{10.4.3}$$

$$B_{\mathrm{DH}} \stackrel{\mathrm{def}}{=} N_{\mathrm{A}} e\left(2\rho_{\mathrm{A}}^*\right)^{1/2}(\epsilon_{\mathrm{r}}\epsilon_0 RT)^{-1/2} \tag{10.4.4}$$

where N_{A} is the Avogadro constant, e is the elementary charge (the charge of a proton), ρ_{A}^* and ϵ_{r} are the density and relative permittivity (dielectric constant) of the solvent, and ϵ_0 is the electric constant (or permittivity of vacuum).

> Lewis and Randall (*J. Am. Chem. Soc.*, 1112–1154, 1921) introduced the term *ionic strength*, defined by Eq. 10.4.2, two years before the Debye–Hückel theory was published. They found empirically that in dilute solutions, the mean ionic activity coefficient of a given strong electrolyte is the same in all solutions having the same ionic strength.

From Eqs. 10.3.8 and 10.4.1 and the electroneutrality condition $\nu_+ z_+ = \nu_- z_-$, we obtain the following expression for the logarithm of the mean ionic activity coefficient of an electrolyte solute:

$$\ln \gamma_\pm = -\frac{A_{\mathrm{DH}} |z_+ z_-| \sqrt{I_m}}{1 + B_{\mathrm{DH}} a \sqrt{I_m}} \tag{10.4.7}$$

In this equation, z_+ and z_- are the charge numbers of the cation and anion of the solute. Since the right side of Eq. 10.4.7 is negative at finite solute molalities, and zero at infinite dilution, the theory predicts that $\gamma_\pm$ is less than 1 at finite solute molalities and approaches 1 at infinite dilution.

Figure 10.4 shows $\ln \gamma_\pm$ as a function of $\sqrt{I_m}$ for aqueous HCl and $CaCl_2$. The experimental curves have the limiting slopes predicted by the Debye–Hückel limiting law (Eq. 10.4.8), but at a low ionic strength the curves begin to deviate significantly from the linear relations predicted by that law. The full Debye–Hückel equation (Eq. 10.4.7) fits the experimental curves over a wider range of ionic strength.