Acid Dissociation Constants; Weak Acids; Debye Huckel Limiting Law

For a weak acid HA in aqueous solution at temperature T and pressure p (which is ambient pressure and so close to the standard pressure) the following chemical equilibrium is established.

\[
\text{HA(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \quad (a)
\]

The r.h.s. of equation (a) describes a 1:1 ‘salt’ in aqueous solution. At equilibrium (i.e. at a minimum in Gibbs energy), the thermodynamic description of the solution takes the following form.

\[
\mu^{\text{eq}}(\text{HA;aq};T;p) + \mu^{\text{eq}}(\text{H}_2\text{O;aq};T;p) = \mu^{\text{eq}}(\text{H}_3\text{O}^+\text{A}^-;\text{aq};T;p) \quad (b)
\]

We express \(\mu^{\text{eq}}(\text{H}_2\text{O;aq};T;p)\) in terms of the practical osmotic coefficient \(\phi\) for the solution.

\[
\mu^{\text{eq}}(\text{H}_2\text{O;aq};T;p) = \mu^*(\text{H}_2\text{O;aq};T;p) - \phi \cdot R \cdot T \cdot M_1 \cdot [m(\text{HA}) + 2 \cdot m_j]^{\text{eq}} \quad (c)
\]

Here \(m_j\) is the molality of the ‘salt’ \(\text{H}_3\text{O}^+\text{A}^-\). The latter yields 2 moles of ions for each mole of \(\text{H}_3\text{O}^+\text{A}^-\). A full description of the solution takes the following form.

\[
\mu^0(\text{HA;aq}) + R \cdot T \cdot \ln[m(\text{HA}) \cdot \gamma(\text{HA}) / m^0]^{\text{eq}} + \mu^*(\text{H}_2\text{O;aq};T;p) - \phi \cdot R \cdot T \cdot M_1 \cdot [m(\text{HA}) + 2 \cdot m_j]^{\text{eq}} = \mu^0(\text{H}_3\text{O}^+\text{A}^-;\text{aq}) + 2 \cdot R \cdot T \cdot \ln[m_j \cdot \gamma_{\text{eq}}]^{\text{eq}} \quad (d)
\]

The practical osmotic coefficient \(\phi\) describes the properties of solvent, water in the aqueous solution; \(\gamma_{\text{eq}}\) is the mean ionic activity coefficient for the ‘salt’ \(\text{H}_3\text{O}^+\text{A}^-\). By definition, if ambient pressure \(p\) is close to the standard pressure \(p^0\), the standard Gibbs energy of acid dissociation,

\[
\Delta_G^0 = \mu^0(\text{H}_3\text{O}^+\text{A}^-;\text{aq};T;p) - \mu^0(\text{HA;aq};T;p) - \mu^0(\text{H}_2\text{O};\lambda;T;p) = -R \cdot T \cdot \ln(K_A^0) \quad (e)
\]

\(K_A^0\) is the acid dissociation constant. Combination of equations (d) and (e) yields equation (f).

\[
K_A^0 = \frac{m(\text{H}_3\text{O}^+\cdot\text{A}^-)^{\text{eq}} \cdot \gamma_{\text{eq}}(\text{H}_3\text{O}^+\text{A}^-)^{\text{eq}} / m^0}{m(\text{HA}) \cdot \gamma(\text{HA}) / m^0}^{\text{eq}} \quad (f)
\]
For dilute aqueous solutions, several approximations are valid. The exponential term and $\gamma(\text{HA})^{eq}$ are close to unity. There are advantages in defining a quantity $K_A^0$ (app). Further, $\gamma_z(\text{H}_3\text{O}^+\text{A}^-)$ is obtained using the Debye - Huckel Limiting Law, DHLL.

By definition, $K_A^0\text{(app)} = \frac{[m(\text{H}^+\text{A}^-)]^{eq}}{m(\text{HA})^{eq}} \cdot m^0$  \hspace{1cm} (g)

Then $\ln K_A\text{(app)} = \ln K_A^0 + 2 \cdot S_\gamma \left( \frac{I}{m^0} \right)^{1/2}$ \hspace{1cm} (h)

In other words, with increase in ionic strength $I$, $K_A\text{(app)}$ increases as a consequence of ion - ion interactions which stabilise the dissociated form of the acid.