

Extrapolation and interpolation methods using ionic equilibrium constants

1. Concentration dependence of ionic activity coefficients in aqueous solutions

Debye-Huckel is the simplest model to describe the concentration dependence of activity coefficients in the aqueous electrolyte solutions.

According to the Debye-Huckel equation, the activity coefficient of a dissociated electrolyte is given by [63 ROB/STO]:

$$\lg \gamma_{\pm} = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + B a \sqrt{I_m}}$$

The upper adequate limit of this equation is $\approx 10^{-2}$ M.

Solution ionic strength I_m is:

$$I_m = \frac{1}{2} \sum_i z_i^2 m_i$$

where m_i = molality. It should be noted that the molarity ionic strength is more often used:

$$I_m = \frac{1}{2} \sum_i z_i^2 c_i$$

In very dilute solutions ($I_m \sim 10^{-3}$ M) the Debye-Huckel equation may be replaced with the Debye-Huckel limiting law:

$$\lg \gamma_{\pm} = -A |Z_+ Z_-| \sqrt{I_m}$$

In later work Huckel took into account cation - anion interactions to give the extended Debye-Huckel equation. This is adequate up to 0.7-0.8 M

$$\lg \gamma_{\pm} = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + B a \sqrt{I_m}} + C I_m$$

The Guntelberg equation has a similar form and is adequate up to 0.1 M [26 GUN]

$$\lg \gamma_{\pm} = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + \sqrt{I_m}} + B' I_m$$

The Scatchard equation is similar and is adequate up to 0.2 M [61 SCA], [70 SCA/RUS], [76 SCA]

$$\lg \gamma_{\pm} = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}}$$

The Guggenheim equation is adequate up to 0.5 M. [35GUG], [55GUG/TUR]

$$\lg \gamma_{\pm} = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + B' I_m$$

Quasi-lattice model of ionic solutions [79 PYT] is the alternative of the limit Debye-Huckel law for the diluted aqueous electrolyte solutions ($I_m \sim 10^{-2}$ M). In this model the electrolyte activity coefficient is

$$\lg \gamma_{\pm} = -\beta C^{1/3}$$

where β - empirical constant, individual for each electrolyte [71 BOK/CON], [63 ROB/STO].

The equation [78 CRU/REN], [95 CHE/CHO]

$$\lg \gamma_{\pm} = AI_m^{1/3} + BI_m$$

is used for the wider concentration range.

The Robinson - Stokes model is a further development of Debye-Huckel ionic solution model [63 ROB/STO]. It takes into account the hydration of ν moles of electrolyte by h moles of solvent

$$\lg \gamma_{\pm} = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + Ba \sqrt{I_m}} - \frac{h}{\nu} \lg a_w - \lg [1 + 10^{-3} M_w (h - \nu) m]$$

where a_w = water activity, M_w = water molar mass, m = molality.

This equation satisfactorily describes the concentration dependence of electrolyte activity coefficient for 1-1-electrolyte up to 4 - 5 M, and for 2-1-electrolyte up to 1.5-1.8 M [85 RAB].

An empirical equation to describe the concentration dependence of the activity coefficient of a 1-1-electrolyte over a wide concentration range at 298 K was proposed by Solovkin [61 SOL], [69 SOL]:

$$\lg \gamma_{\pm} = \frac{-0.5091 C^{1/2}}{1 + 0.3286 a_{\pm} C^{1/2}} + B_{\pm} C + D_{\pm} C^{(r_- - r_+)/r_+}$$

where «+» and «-» correspond to cation and anion; C = molarity; a_{\pm} = " effective radius " of hydrated ion.

The Davies equation [62 DAV] is often used for describe the concentration dependence of activity coefficients

$$\lg \gamma_i = -A_{\gamma} |Z_+ Z_-| \left(\frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.3 I_m \right)$$

It should be noted that in early works a less suitable value of 0.2 was used instead 0.3 value.

The SIT (Specific Interaction Theory) equation of the generalized inter-ion interaction Bronsted - Guggenheim - Scatchard theory [80 CIA], [90 CIA], [97 GRE/PLY] is often used for the description of the concentration dependence of the ionic activity coefficients in wide concentration range: for 1-1-electrolyte up to 4-4.5 M and for 2-1, 1-2 - electrolytes up to 2-2.5 M. For example, the activity coefficient of M cation in MX electrolyte solution may be calculated as:

$$\lg \gamma_M = \frac{-A_{\gamma} |Z_+ Z_-| \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + \varepsilon_{(M,X,I_b)} m_X$$

The Vasil'ev equation is similar [62 VAS], [82 VAS] :

$$\lg \gamma_M = \frac{-A_\gamma |Z_+ Z_-| \sqrt{I_m}}{1 + 1.6 \sqrt{I_m}} + b_{(M, X, I_b)} I_m$$

Helgeson [81 HEL/KIR] has proposed a semi-empirical method to describe the concentration dependence of activity coefficients, taking ionic hydration, temperature and pressure variations into account:

$$\lg \gamma_\pm = \frac{-A_\gamma |Z_+ Z_-| \sqrt{I_m}}{1 + B_\gamma a \sqrt{I_m}} - \lg[1 + 0.0180153 m] + b_\gamma I_m$$

$$b_\gamma = \frac{(b_{MX}^0 + 2\nu_M \nu_X b_{MX}^1)}{\nu}, \quad \nu = \nu_M + \nu_X.$$

where

$-\lg[1 + 0.0180153 m]$ is term of mole fraction – molality conversion;

b_{MX}^0, b_{MX}^1 are inter-ion interaction parameters.

Bromley [73 BRO] has proposed a general equation to calculate activity coefficients in aqueous solutions over a wide concentration range up to 6-8 molality

$$\log \gamma_\pm = \frac{-A_\gamma |Z_+ Z_-| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(B_0 - B)I}{(1 + \alpha I)^n} + BI + CI^2$$

where ρ is an empirical constant, individual for each electrolyte type, α = “effective ionic radius”, B, C are parameters, individual for each electrolyte, B_0, n are characteristic constants.

For practical purposes Bromley [73 BRO] simplified this equation to:

$$\log \gamma_\pm = \frac{-A_\gamma |Z_+ Z_-| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6B)|Z_+ Z_-| I}{\left(1 + \frac{1.5}{|Z_+ Z_-|} I\right)^2} + BI$$

Later it was found, that the B values for individual electrolytes can be approximated to a simple function from values of individual ions

$$B = B_{cation} + B_{anion} + \delta_{cation} \delta_{anion}.$$

Taking ionic association in high concentration ranges into account, the Bromley equation (for symmetric 1-1 and 2-2-electrolytes) becomes [73 BRO]:

$$\lg \gamma_\pm = \frac{-A_\gamma |Z_+ Z_-| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6B)|Z_+ Z_-| I}{\left(1 + \frac{1.5}{|Z_+ Z_-|} I\right)^2} + BI - E \alpha I^{1/2} \left[1 - e^{-\alpha I^{1/2}}\right]$$

Zemaitis [86 ZEM/CLA] modified the Bromley equation to :

$$\log \gamma_\pm = \frac{-A_\gamma |Z_+ Z_-| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6B)|Z_+ Z_-| I}{\left(1 + \frac{1.5}{|Z_+ Z_-|} I\right)^2} + BI + CI^2 + DI^3,$$

where B , C , D are temperature - dependent parameters, individual for each electrolyte

$$B = B_1 + B_2T + B_3T^2$$

$$C = C_1 + C_2T + C_3T^2$$

$$D = D_1 + D_2T + D_3T^2$$

T = temperature $^{\circ}\text{C}$.

Madariaga et al. [94 CAS/ETX], [96 BOR/CAS] modified the Bromley equation to :

$$\log \gamma_M = \frac{-A_\gamma z_M^2 I_m^{1/2}}{1 + I_m^{1/2}} + \sum^0 B(|z_M| + |z_X|)^2 m / 4$$

$$^0 B = + \frac{(0.06 + 0.6B_{MX})|Z_+ Z_-|}{\left(1 + \frac{1.5}{|Z_M Z_X|} I_m\right)^2} + B_{MX}$$

Virial expansions of ionic strength effects (on the basis of the extended Debye-Huckel model) are often used to describe the concentration dependence of activity coefficients in aqueous solutions [57 MAC], [76 SCA]

$$\lg \gamma_{\pm} = \frac{-A_\gamma |Z_+ Z_-| \sqrt{I_m}}{1 + Ba\sqrt{I_m}} + CI_m + DI_m^{3/2}$$

$$\lg \gamma_{\pm} = \frac{-A_\gamma |Z_+ Z_-| \sqrt{I_m}}{1 + Ba\sqrt{I_m}} + CI_m + DI_m^{3/2} + EI_m^2$$

The Li - Page [98 LI/PAG] equation describes the concentration dependence of activity coefficient in electrolyte aqueous solution, taking into account solvation effects

$$\frac{1}{n} \sum_{i=1}^n \ln \gamma_i = \alpha I \left(\frac{2}{3} \sqrt{\frac{I}{I_{cr}}} - 1 \right)$$

where n = the particle number,

I_{cr} = the critical value of the ionic strength, at which the natural logarithm of electrolyte activity coefficient begins to increase;

α is an empirical parameter.

Hamer and Wu proposed a type of virial equation to calculate activity coefficients [72 HAM/WU]

$$\lg \gamma_{\pm} = \frac{-AI_m^{1/2}}{(1 + BI_m^{1/2})} + \beta I_m + CI_m^2 + DI_m^3$$

where $A=0.5108$; B , β , C , D are parameters, individual for each electrolyte.

Pan [81 PAN] has offered the simple modification of Robinson - Stokes equation [48 STO/ROB] (for univalent electrolytes)

$$\ln \gamma_{\pm} = -\frac{\alpha m^{1/2}}{1 + \beta \alpha^* m^{1/2}} + 2M_1(h-1)m$$

where $\alpha = 1,17444$; α^* is an individual electrolyte parameter; h is the hydration number.

Chen [82 CHE/BRI] proposed the following equation to calculate the activity coefficient for univalent electrolytes on a mole fraction basis

$$\ln \gamma_{\pm} = (\ln \gamma_{x,c} + \ln \gamma_{x,a})/2 - \ln(1 + 2M_1m)$$

$$\ln \gamma_{x,c} = \ln \gamma_{\pm a} = \ln \gamma_i^{\text{pdh}} + \ln \gamma_i^{\text{lc}}$$

where

$$\ln \gamma_i^{\text{pdh}} = -[A\phi/(M_1)^{1/2}][2 \ln(1 + \rho I_x^{1/2})/\rho + (I_x^{1/2} - 2I_x I_x^{1/2})/(1 + \rho I_x^{1/2})]$$

$$I_x = (x_c + x_a)/2 = x$$

$$\ln \gamma_i^{\text{lc}} = x_1^2 \tau_1 e^{-\alpha \tau_1} / (2x e^{-\alpha \tau_1} + x_1)^2 - x x_1 \tau_2 e^{-\alpha \tau_2} / (x + x_1 e^{-\alpha \tau_2})^2 + x_1 \tau_2 e^{-\alpha \tau_2} / (x + x_1 e^{-\alpha \tau_2}) - \tau_2 - \tau_1 e^{-\alpha \tau_1}$$

Here $A\phi = 0,392$; $\rho = 14,9$; $a = 0,2$; x_a , x_c , x_1 = mole fractions of anion, cation and water.

Meisner and Kusik [78 KUS/MEI] proposed the following equation to calculate activity coefficients:

$$\gamma_{\pm} = \{1 + B[1 + 0.1(m/m^{\circ})]^q - B\} \gamma^*$$

where

$$B = 0.75 - 0.065q$$

$$\log \gamma^* = -A_{\gamma} m^{1/2} / [1 + C(m/m^{\circ})^{1/2}]$$

$$C = 1 + 0.055q e^{-0.023(m/m^{\circ})^3}$$

and $A_{\gamma} = 0.5107$; q is a parameter, individual for each electrolyte.

Bahe [72 BAH] proposed equation to calculate activity coefficients in molarity units:

$$\lg \gamma_{\pm} = -A I_c^{1/3} + B I_c - \lg(1 + 2M_1m)$$

where $A = 0.28894$; B is a parameter, individual for each electrolyte.

More recently, the following equation has been proposed [96 KHO/VER], [99 TAG/MOD]:

$$\ln \gamma_i = \frac{-A_x z_i^2 \sqrt{I_x}}{1 + p \sqrt{I_x}} + B_i \frac{I_x^{3/2}}{1 + p \sqrt{I_x}} + C_i \ln \left(1 + p I_x^{2/3} \right)$$

This describes the activity coefficients for 1-, 2-, 3-charged ions in the mole fraction scale with reasonable precision.

Kuznetsova has proposed an original equation, based on a quasi-crystalline model of electrolyte solutions [82 KUZ], [93 KUZ]

$$\ln \gamma_{\pm} = z_+ z_- q \left[-0.89565 m^{1/3} / \nu^{2/3} + 0.0095806 (d_0^2 - \Phi / d_0) m + 0.00094395 \nu^{1/3} \Phi m^{4/3} \right]$$

where

$$\Phi = \alpha_+ \nu_- / \nu_- + \alpha_- \nu_+ / \nu_+ \quad \text{и} \quad q = \left(z_+ z_- \frac{(\nu_+ + \nu_-)}{2} \right)^{1/2}$$

α = ion polarizability,

ν = the number of ions in the electrolyte formula,

q is the generalized electrolyte charge,

d_0 = distance between the ions in the electrolyte quasi-crystalline lattice.

The Pitzer equations [73 PIT], [91 PIT] are widely used to describe the concentration dependence of activity coefficient. For example, for MX, the activity coefficient is expressed as [73 PIT/MAY]:

$$\ln \gamma_{MX} = |Z_M Z_X| f^\gamma + m \frac{(2\nu_M \nu_X)}{\nu} B_{MX}^\gamma + m^2 \left(\frac{2(\nu_M \nu_X)^{3/2}}{\nu} \right) C_{MX}^\gamma$$

where ν_M and ν_X = the number of M and X ions in the electrolyte formula $M\nu_M X\nu_X$,

Z_M, Z_X = the ion charge, m = molality,

$\nu = \nu_M + \nu_X$.

For aqueous solutions at 25⁰ C and 10⁵ pascals, the following equations may be used

$$f^\gamma = -0.392 \left(\frac{\sqrt{I_m}}{1 + 1.2\sqrt{I_m}} + 1.667 \ln(1 + 1.2\sqrt{I_m}) \right)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + \frac{\beta_{MX}^{(1)}}{2I_m} \left(1 - (1 + 2\sqrt{I_m} - 2I_m) e^{-2\sqrt{I_m}} \right)$$

$$C_{MX}^\gamma = \frac{3}{2} C_{MX}^\phi$$

where f^γ = Debye-Huckel term, which is extended by addition the osmotic effects;

parameters $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ characterize the second virial coefficient (they correspond to the ε – coefficient in SIT equation); C_{MX}^ϕ determines the third virial coefficient.

Ionic strength in Pitzer equations is calculated in molality units. The Pitzer equation is easily extended for electrolyte mixture, however, at the present time, Pitzer parameters are known for only a few binary electrolytes.

The Pitzer equation to calculate the activity coefficients for $C_x A_y$ in an electrolyte mixture is [91 PIT]

$$\begin{aligned}
\ln \gamma_C &= z_C^2 F + \sum_a m_a (2 B_{Ca} + Z C_{Ca}) + \sum_c m_c \left(2 \Phi_{Cc} + \sum_a m_a \Psi_{Cca} \right) \\
&\quad + \sum_a \sum_{a'} m_a m_{a'} \Psi_{aa'C} + |z_C| \sum_c \sum_a m_c m_a C_{ca} \\
\ln \gamma_A &= z_A^2 F + \sum_c m_c (2 B_{cA} + Z C_{cA}) + \sum_a m_a \left(2 \Phi_{Aa} + \sum_c m_c \Psi_{CaA} \right) \\
&\quad + \sum_c \sum_{c'} m_c m_{c'} \Psi_{cc'A} + |z_A| \sum_c \sum_a m_c m_a C_{ca}
\end{aligned}$$

where

$$\begin{aligned}
F &= -A_\phi \left(\frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2 I^{1/2}) \right) + \sum_c \sum_a m_c m_a B'_{ca} \\
&\quad + \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_a \sum_{a'} m_a m_{a'} \Phi_{aa'} \\
C_{CA} &= C_{CA}^\phi / 2 |z_C z_A|^{1/2} \\
Z &= \sum_c |z_c| \cdot m_c + \sum_a |z_a| \cdot m_a; \\
B_{CA}^\phi &= \beta_{CA}^{(0)} + \beta_{CA}^{(1)} e^{-\alpha_{CA} \sqrt{I}} \\
B_{CA} &= \beta_{CA}^{(0)} + \beta_{CA}^{(1)} g(\alpha_{CA} \sqrt{I}) \\
B'_{CA} &= \beta_{CA}^{(1)} g'(\alpha_{CA} \sqrt{I}) / I
\end{aligned}$$

and functions $g(x)$ and $g'(x)$ are

$$\begin{aligned}
g(x) &= 2(1 - (1 + x)e^{-x})/x^2 \\
g'(x) &= -2 \left(1 - \left(1 + x + \frac{x^2}{2} \right) e^{-x} \right) / x^2
\end{aligned}$$

where $x = \alpha \sqrt{I_m}$, $\alpha = 2$.

Edwards has simplified these equations, taking binary inter-ion interactions only into account. [78 EDW/MAU]

$$\begin{aligned}
\ln \gamma_i &= -A_\phi(T) \cdot z_i^2 \left(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right) \\
&\quad + 2 \cdot \sum_{j \neq \text{H}_2\text{O}} m_j \left(\beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha^2 I} (1 - (1 + \alpha\sqrt{I}) \exp(-\alpha\sqrt{I})) \right) \\
&\quad - \frac{z_i^2}{\alpha^2 I^2} \sum_{j \neq \text{H}_2\text{O}} \sum_{k \neq \text{H}_2\text{O}} m_j m_k \beta_{jk}^{(1)} \left(1 - \left(1 + \alpha\sqrt{I} + \frac{1}{2} \alpha^2 I \right) \exp(-\alpha\sqrt{I}) \right)
\end{aligned}$$

where

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

A_ϕ = Debye-Huckel parameter; β^i = Pitzer parameter of binary interactions.

Milero has proposed a simplified Pitzer-type equation [82 MIL/SCR], [92 MIL]:

$$\ln \gamma_i = Z_i^2 f^\gamma + B_i^0 I_m + B_i^1 f^1 + C_i I_m^2$$

$$f^\gamma = -0.392 \left(\frac{\sqrt{I_m}}{1 + 1.2\sqrt{I_m}} + \left(\frac{2}{1.2} \right) \ln(1 + 1.2\sqrt{I_m}) \right)$$

$$f^1 = \left[(1 - \exp(-2\sqrt{I_m})) (1 + 2\sqrt{I_m} - 2I_m) \right]$$

Setchenow has proposed the following equation to calculate the concentration dependence of activity coefficient of neutral particles [89 SET]:

$$\ln \gamma_N = \frac{S_0}{S_S} = km_S$$

where

S_0 = solubility in the pure water;

S_S = solubility in the electrolyte solution;

k = desalt coefficient, so-called Setchenow coefficient;

m_s = electrolyte concentration.

The applicability of the Setchenow equation is limited, as the k -coefficient is assumed to be temperature - independent.

For concentrated solutions Cramer has added a second virial coefficient to the Setchenow equation [80 CRA]:

$$\ln \gamma_N = \frac{S_0}{S_S} = km_S + k_1 m_S^2$$

Pitzer has proposed a more precise equation which takes temperature effects and the influence of electrolyte background into account [74 PIT], [75 PIT], [77 PIT], [78 PIT]

$$\ln \gamma_N = 2\beta_{0(m-m)}m + 2\beta_{0(m-S)}m_S$$

where

$\beta_{0(m-m)}$ = temperature - dependent parameter, which reflects the intermolecular interactions;

$\beta_{0(m-S)}$ = temperature - dependent parameter, which reflects the ion –molecular interactions;

m_S = concentration of neutral particles.

In an electrolyte mixture, containing n_{cat} cations and n_{an} anions, the equation to calculate the activity coefficient of a neutral particle N is [91 PIT]:

$$\ln \gamma_N = \sum_{i=1}^{n_{cat}} m_{cat.} (2\lambda_{N_{cat}}) + \sum_{j=1}^{n_{an}} m_{an.} (2\lambda_{N_{an}}) + \sum_{i=1}^{n_{cat}} \sum_{j=1}^{n_{an}} m_{cat} m_{an} \zeta_{cat-an}$$

where λ , ξ are Pitzer coefficients.

2. Equations used to recalcule equilibrium constants to a standard state

Most often the following equations are used to express the dependence of conditional equilibrium constant or concentration equilibrium constant on ionic strength [62 VAS], [82 VAS]

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + BaI^{1/2})}$$

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + BaI^{1/2})} + CI$$

where

$$\Delta z^2 = \sum z_{\text{reaction products}}^2 - \sum z_{\text{reagents}}^2$$

These equations follow from the Debye-Huckel theory.

The Guggenheim equation is similar [55 GUG/TUR]:

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + cI^{1/2})} + \varepsilon_i I$$

where c is a variable parameter;

ε_i is a characteristic parameter of complex formation reaction.

A simplified form of this equation has been proposed [90 WOO], [00 GAM/WOO], [98 DEB/CAS]

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + I^{1/2})} + bI$$

The following equation has been proposed to calculate the protonation constants for mono- and amino-acids in the concentration range $m < 2$ of an electrolyte MX on the basis of Guggenheim method [93 BRA/ARC], [00 BAR/BRA]

$$pK = pK^T - \frac{A\sqrt{I}}{1 + B_{HX}\sqrt{I}} - \frac{A\sqrt{I}}{1 + B_{MA}\sqrt{I}} + (C_{HX} + C_{MA} - \lambda_{HA,MX})$$

In the Scathard model, the dependence of a concentration the constant on ionic strength is described by the following equation [61SCA], in which the ionic strength effect is expanded to a higher degree:

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + a_J I^{1/2})} + P_i I + Q_i I^2 + R_i I^3$$

where

a_J = variable parameter, which is often accepted by default $a_J = 1.5$;

P_i , Q_i are empirical parameters for given complex formation reaction.

For a wide concentration range of background electrolyte it is preferable to use the following equation, which is extended by virial Debye-Huckel terms [96 PEZ/MOL]

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + BaI^{1/2})} + CI + DI^{3/2}$$

The modified forms of this equation were used in [97 LI/BYR], [00 KLU/BYR], [91 KIS/SOV]

$$\lg K = \lg K^T - \frac{AI^{1/2}}{(1 + BI^{1/2})} + CI$$

$$\lg K = \lg K^T - \frac{AI^{1/2}}{(1 + BI^{1/2})} + CI + DI^{3/2}$$

For a long time it was believed that equilibrium constants up to 0.5-0.6 M of ionic strength could be calculated by either the Davies equation [62 DAV]

$$\lg K = \lg K^T - \Delta z^2 A_\gamma \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.2I \right)$$

or the equation [82 VAS]

$$\lg K = \lg K^T - \Delta z^2 A_\gamma \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right)$$

Vasil'ev has proposed an equation with one empirical parameter for the calculation the dissociation (stability) constants in aqueous solutions [62 VAS]

$$\lg K = \lg K^T - \frac{A_\gamma \Delta z^2 I^{1/2}}{(1 + 1.6I^{1/2})} + bI$$

Later this was modified to [82 VAS]

$$\lg K = \lg K^T - \Delta z^2 A_\gamma \left(\frac{I^{1/2}}{1 + 1.6I^{1/2}} - 0.05I \right) + \delta I$$

Recently it has been used to study the dependence of stability constant in aqueous solutions on ionic strength on the basis of the extended Debye-Huckel equation [97 DAN/DES]:

$$\lg K = \lg K^T - \frac{z^* I^{1/2}}{(2 + 3I^{1/2})} + CI + DI^{3/2} + EI^2$$

where

$$z^* = \sum (\text{charges})_{\text{products}}^2 - \sum ((\text{charges})_{\text{reagents}}^2)$$

K^T = thermodynamic stability constant (ionization constant) at infinite dilution;
C,D,E are empirical parameters. At $I < 1$ M the EI^2 term is neglected.

At $K > 0.2$

$$C = 0.1p^* + 0.20z^*$$

$$D = -0.075z^*$$

where

$$p^* = \sum (\text{moles})_{\text{ion reagents}} - (\text{moles})_{\text{products}}$$

Later an alternative equation was proposed to perform calculations in solutions with moderately concentrated background concentrations of electrolytes, including and mixtures (e.g. synthetic sea water and mineralized water) [99 DES/GIA]

$$\lg K = \lg K^T - \left[\frac{I^{1/2}}{(2 + 3I^{1/2})} + 0.1I^{3/2} \right] + CI$$

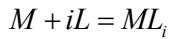
where

$$C = 0.1p^* + 0.23z^*,$$

$$z^* = \sum (\text{charge})_{\text{ion reagents}}^2 - \sum (\text{charge})_{\text{products}}^2$$

$$p^* = \sum (\text{moles})_{\text{ion reagents}} - (\text{moles})_{\text{products}}$$

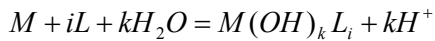
In the SIT theory the following equation may be used to extrapolate and interpolate ionic equilibrium constants. For example, for complex formation reaction:



$$\lg K = \lg K^T + \frac{A_\gamma \Delta z^2 I_m^{1/2}}{(1 + 1.5I_m^{1/2})} - \Delta \varepsilon I_m$$

where $\Delta \varepsilon = \varepsilon_{ML_i} - \varepsilon_M - i\varepsilon_L$ and $\Delta z^2 = z_{ML_i}^2 - z_M^2 - z_L^2$.

For the reaction



the SIT equation becomes:

$$\lg K = \lg K^T + \frac{A_\gamma \Delta z^2 I_m^{1/2}}{(1 + 1.5I_m^{1/2})} - \Delta \varepsilon I_m - k \lg a_w$$

The quasi-lattice model for the dependence of stability constant on ionic strength may be reduced to the following expression [97 VIL/FIO], [97 VIC]

$$\lg K = \lg K^T - \Delta z^2 a \sqrt[3]{I} + bI$$

In the low concentration range up to 0.5 M It is possible to use the following equation to describe the concentration dependence of stability constants of mono-ligand complexes [80 SUN/HAR]

$$\lg K = \lg K^T - 0.51 \left[\left(\frac{\sqrt{I}}{1 + 1.5\sqrt{I}} \right) - 0.09 \right] \chi + 0.09I$$

Baes and Mesmer [76 BAE/MES] modified the Guggenheim equation by including the B_{MX} parameter as a function of ionic strength. It gives the following expression for concentration dependence of stability constant:

$$\lg \beta(I_{m,n}) - \Delta z_i^2 \frac{0.511 \sqrt{I_{m,n}}}{1 + \sqrt{I_{m,n}}} - r \lg a_w = \lg \beta^0 + \Delta B^\infty [1 - F(I_{m,n})] I_{m,n} + \Delta B^0 F(I_{m,n}) I_{m,n}$$

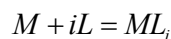
where

$$B_{MX} = B_{MX}^\infty + (B_{MX}^0 - B_{MX}^\infty) F(I_m)$$

$$F(I_m) = \frac{1 - (1 + 2\sqrt{I_m} - 2I_m) e^{-2\sqrt{I_m}}}{4I_m}; \quad F(0) = 1; \quad F(\infty) = 0$$

The B_{MX}^0 and B_{MX}^∞ parameters are estimated from the concentration dependence of activity coefficients.

An advanced model of the modified Bromley [99 RAP/SAN], [99 BEL/OLA] methodology gives the following expression for concentration dependence of stability constant for reaction



$$\lg \beta_i = \lg \beta_i^0 + (i^2 - 7i)D + F_M + iF_L - F_{ML_i}$$

where

F_i – cross-interaction coefficients with the ions of background XY electrolyte, for example, for metal ion

$$F_M = \sum_X \left(\frac{0.06 + 0.6 B_{MX}}{\left(1 + \frac{1.5 I_m}{|z_M z_X|} \right)} + B_{MX} \right) \frac{(|z_M z_X|)}{4} I_m$$

Application of the Pitzer theory for the extrapolation and interpolation of ionic equilibrium constants may be reduced to the multi-parametrical virial equation [91PIT]:

$$\lg K = \lg K^T + \Delta z^2 f^{(\gamma)} - A_i I + C_i I^2 + B_i \left[1 - (1 + 2\sqrt{I}) e^{-2\sqrt{I}} \right] + \Delta z^2 \frac{\beta_{MX}}{\ln 10} f^1$$

where

$$f^{(\gamma)} = -0.392 \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1+1.2\sqrt{I}) \right]$$

$$f^1 = \left[-1 + (1 + 2\sqrt{I} + 2I)e^{-2\sqrt{I}} \right]$$

On the basis of the Pitzer theory Bugaevsky [87 BUG/HOL] proposed the following equation:

$$\lg K_C + (0.39211 \Delta z^2 / \ln 10) \left[I^{1/2} (1 + 1.2 I^{1/2}) + \frac{5}{3} \ln(1 + 1.2 I^{1/2}) \right] = \lg K^T + A_1 I + A_2 I^2$$

To calculate the protonation constants for mono- and aminoacids in the concentration range $m < 2$ (MX electrolyte) the following equation has been proposed [93 BRA/ARC], [00 BAR/BRA], on the basis of the Pitzer method:

$$pK = pK^T + \frac{2}{\ln 10} f^\gamma + \frac{2\beta_{MX}^1}{\ln 10} I e^{-2\sqrt{I}} + AI + B \left[1 - (1 + 2\sqrt{I})e^{-2\sqrt{I}} \right]$$

where

$$f^\gamma = -0.3910 \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1+1.2\sqrt{I}) \right]$$

$$A = 2 \frac{(\beta_{HX}^0 + \beta_{MA}^0 - \lambda_{AH,MX}^0)}{\ln 10}$$

$$B = 2 \frac{(\beta_{HX}^1 + \beta_{MA}^1 - \beta_{MX}^1)}{\ln 10}$$

A simplified version of the Pitzer equation has been proposed to describe the concentration dependence of protonation constants of carboxylic acids [97 FOT/GIA], [98 FOT/SAM]

$$\ln K_j = \ln K_j^0 - 2z_A f^\gamma + P_1 I + P_2 I^2 + P_3 f_1$$

where P_1 , P_2 , P_3 are empirical parameters and

$$f^\gamma = -0.392 \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1+1.2\sqrt{I}) \right]$$

$$f_1 = \left[-1 + (1 + 2\sqrt{I} + 2I)e^{-2\sqrt{I}} \right]$$

Partanen has modified the Pitzer equation to describe the concentration dependence of protonation constants for carboxylic acids [00 PAR/JUU], [00 PAR]

$$\ln K_{m,MX} = \ln K_a + \alpha(I_m)^{1/2} \left[\frac{1}{\left(1 + B_H(I_m)^{1/2}\right)} + \frac{1}{\left(1 + B_A(I_m)^{1/2}\right)} \right] - \frac{(b_{H,MX} + b_{A,MX})I_m}{m^0}$$

where B_i , b_i parameters are depending on ion kinds and background electrolyte;
 m^0 standard ionic strength.

For practical purposes, Millero has proposed the simplified Pitzer type equation [82 MIL/SCH], [92 MIL]

$$\lg K = \lg K^T + \Delta z^2 f^\gamma + B^0 I + f^1 B^1 + C I^2$$

$$f^\gamma = -0.392 \left[I^{1/2} / (1 + 1.2 I^{1/2}) + (2/1.2) \ln(1 + 1.2 I^{1/2}) \right]$$

$$f^1 = \left[1 - (1 + 2\sqrt{I} + 2I) e^{-2\sqrt{I}} \right]$$

The following method was proposed to recalculate the protonation constants for the aqua - organic electrolyte solutions [90 LED/SHA]

$$\lg K_C - bI = \lg K^T + \frac{A^* I^{1/2}}{(1 + I^{1/2})}$$

where A^* and b are empirical parameters.

A virial expansion has been used to describe the dependence of dissociation constants for polyelectrolytes on ionic strength [99 DAN/DES]

$$\lg K = \lg K^T + \alpha_1 \sqrt{I} + \alpha_2 I + \alpha_3 I^2$$

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