

Activity and activity coefficients VI: Specific ion interaction

Part II of this series attempted to present an intuitive understanding of the Debye-Hückel equation for calculation of the activity coefficient (γ) of an ion in solution. That equation includes a term for ionic strength (I), the nature of which was discussed in the Part III of this series. Part III pointed out that ionic strength takes into account only the charge of ions, rather than their ionic potential (charge ÷ radius) or their position in spectrum from hard to soft ions. We might rigorously prefer an approach that considered the interactions of our ion of interest with each of the specific ions in the solution.

Specific ion interaction theory does just that, as shown below. Here, the equation for γ includes terms for each interaction of our ion of interest with ions of opposite charge. As a geochemical example, in calculating γ for

Mg²⁺ in a solution, we would want to consider the deactivating effects of pairing with some of the following anions:

Ion of interest <i>i</i>	Counterion <i>j</i>	Interaction term <i>ij</i>
Mg ²⁺	HCO ₃ ⁻	$\epsilon_{Mg^{2+} - HCO_3^-}$
Mg ²⁺	CO ₃ ²⁻	$\epsilon_{Mg^{2+} - CO_3^{2-}}$
Mg ²⁺	SO ₄ ²⁻	$\epsilon_{Mg^{2+} - SO_4^{2-}}$
Mg ²⁺	PO ₄ ³⁻	$\epsilon_{Mg^{2+} - PO_4^{3-}}$
Mg ²⁺	F ⁻	$\epsilon_{Mg^{2+} - F^-}$
Mg ²⁺	Cl ⁻	$\epsilon_{Mg^{2+} - Cl^-}$
Mg ²⁺	Br ⁻	$\epsilon_{Mg^{2+} - Br^-}$
Mg ²⁺	Oxalate	$\epsilon_{Mg^{2+} - Ox^-}$

In our calculation of γ for our ion of interest *i*, we would need to use each of these terms, multiplied times the concentration of each counterion *j*, and then sum to find their combined effect, as shown below.

$$\log(\gamma_i) = -z_i^2 \frac{0.51 \sqrt{I}}{1 + 1.5 \sqrt{I}} + \sum_{j=1}^n \epsilon_{ij} m_j$$

Equation using specific ion interaction theory :

Charge on ion of interest *i*

Debye-Hückel term

Term for interaction between ion of interest *i* and each counterion *j*

Concentration of each counterion *j*