

Application of the Brønstedt-Guggenheim-Scatchard Specific Ion Interaction Theory to the Concentration Dependence of Complexation Constants in NaCl Solutions up to the Saturation of Halite

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There are numerous methods for estimating activity coefficients of aqueous species in electrolyte solutions. While the application of the simplest models requiring no empirical parameters is restricted to very low ionic strengths (e.g., $I < 0.1$ mol/kg for the Debye-Hückel equation and $I < 0.3$ mol/kg for the Davies equation), more elaborate models like the Pitzer equations extend the range of application to concentrated salt solutions but only at the cost of requiring a large number of empirical parameters which must be obtained from experimental data. The Brønstedt-Guggenheim-Scatchard specific ion-interaction theory (SIT) (Grenthe et al., 1997) takes an intermediate position in that it requires only a minimum number of empirical parameters but it is commonly considered to be restricted to ionic strengths below about 3.5 mol/kg. According to the SIT model, the activity coefficient of an ion i with charge Z_i is given by

$$\log \gamma_i = -Z_i^2 D + \sum_k \epsilon(i, k) m_k$$

where D is a particular form of the Debye-Hückel term with a constant ion size parameter and $\epsilon(i, k)$ is the specific ion interaction coefficient between ions i and k (zero for ions of the same charge sign). With this SIT model for activity coefficients, the relation between concentration equilibrium constants ($\log K$) and thermodynamic equilibrium constants ($\log K^\circ$) of a reaction in an ionic medium of molality m is given by

$$\log K = \log K^\circ + *(Z^2)D - *\epsilon m$$

where $*(Z^2)$ is a sum function of the squared charges of the reacting ionic species and $*\epsilon$ is a sum function of the interaction parameters between the reacting species and the ionic medium (assuming that only interactions between the reacting species and the ionic medium are significant).

Using SIT to model the concentration dependence of the concentration constants of complex formation reveals that, at least in the case of NaCl solutions, SIT can be used at much higher ionic strengths than is commonly believed. Fanghänel et al. (1999) determined the stepwise formation constants (in terms of concentrations) of Cm(III) carbonate complexes (1:1 to 1:4) in aqueous NaCl solutions with m_{NaCl} ranging from 0 to 6 mol/kg. An SIT fit to these data with only two free parameters per equilibrium ($*\epsilon$ and $\log K^\circ$) gives an excellent representation of the experimental data across the entire range of NaCl concentrations (see Figure 1), even at very high concentrations near the saturation of halite (6.15 mol/kg). A similar picture emerges from SIT fits to the concentration dependence of, e.g., the complexation

constants of Cm(III) fluoride 1:1 (0 - 5 mol/kg NaCl) and of Cm(III) hydroxide 1:1 and 1:2 (0 - 6 mol/kg NaCl), of neptunyl and uranyl EDTA complexation (0.3 - 5 mol/kg NaCl), and of the first dissociation constant of aqueous H_2S (0.1 - 6 mol/kg NaCl).

The large validity range of the SIT model suggests that it could be used for the modelling of saline groundwater at high concentrations instead of the Pitzer equations, as long as NaCl makes the dominant contribution to the ionic strength. This would afford a considerable simplification of modelling, as fewer empirical parameters would be needed.

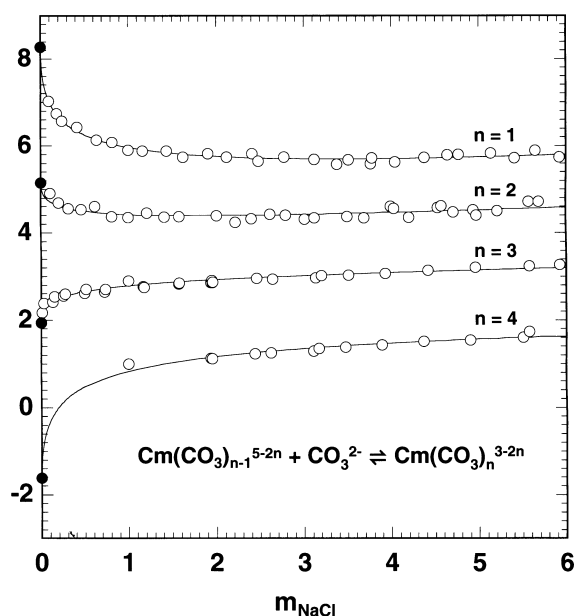


Figure 1: Concentration dependence of the formation constants of Cm(III) carbonate complexes at 25 °C. The SIT model (filled circles and curves) gives an excellent fit to the experimental data (open circles) by Fanghänel et al. (1999), ranging from dilute to concentrated NaCl solutions. Note that the precipitation of halite starts at about 6.15 mol/kg.

Fanghänel Th, Könnecke Th, Weger H, Paviet-Hartmann P, Neck V & Kim JI, *J. Solution Chem.*, **28**, 447-462, (1999).
Grenthe I, Plyasunov AV & Spahiu K, *Modelling in Aquatic Chemistry, NEA/OECD*, 325-426, (1999).