Thermodynamics of Saturated Lanthanide Nitrate-Water Systems

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The thermodynamic properties of saturated aqueous lanthanide nitrate solutions were determined using recently published critically evaluated solubility and activity data. The variation of the thermodynamic functions and congruent melting points as a function of atomic number are interpreted in terms of changes in inner sphere coordination number in both the solid hexahydrates and in the aquo ions, and in terms of the double-double effect. Inconsistencies in experimental solubility data are generally caused by uncertainties in solid phase composition which is shown to be due to the very small Gibbs energies accompanying transitions from stable to metastable systems differing in the number of hydrating water molecules.

KEY WORDS: Lanthanide nitrates; hydrates; solubilities; activities; solvation energies; phase transitions; congruent melting points; specific solvation; metastable equilibria; tetrad effect; double-double effect.

1. INTRODUCTION

The aqueous solubilities of highly soluble salts are governed not only by differences between Gibbs energies of hydration and Gibbs lattice energies, but also by ion-ion interactions, ion-dipole and multipole interactions, and competition between ions for water molecules. Lanthanide nitrates constitute a particularly convenient example for determining the various factors influencing their solubilities, and in particular for studying changes in these contributions with changes in ionic size. The bases for determining the thermodynamic properties of


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these highly soluble salts lie in the availability of accurate solubility data and activity coefficients which have only recently become available.

All aqueous solubility data inclusive of 1982 have recently been critically evaluated. In this critical evaluation, the various experimental data were compared and, when possible, fitted by a weighted least squares method to the following smoothing equation

\[ Y = a + b/T + c \ln T \]  

where \[ Y = \ln \left( \frac{m}{m_o} \right) - nM_2(m - m_o) \]  

In this equation \( n \) is the hydration number of the solid phase hydrate, \( m \) is the solubility in mol-kg\(^{-1}\) at temperature \( T \) (K), \( m_o \) is an arbitrarily selected reference molality (usually the solubility at 25°C), \( M_2 \) is the molar mass of water, and \( a, b, \) and \( c \) are constants. With sufficiently accurate solubility data, Eq. (1) also permits one to calculate accurate congruent melting points, i.e., the temperature at which the solid hydrate melts in its own waters of hydration, and at which point the solubility in water is simply \( 55.508/n \) mol-kg\(^{-1}\). The computed thermodynamic functions of saturated lanthanide nitrate solutions are based on the following considerations.

The aqueous solubility of a lanthanide nitrate hydrate can be described by the schematic reaction

\[ \text{Ln(NO}_3\text{)}_3 \cdot n\text{H}_2\text{O(s)} = \text{Ln(NO}_3\text{)}_3\text{(aq)} + n\text{H}_2\text{O(aq)} \]

\[ = \text{Ln}^{3+}\text{(aq)} + 3\text{NO}_3\text{(aq)} + n\text{H}_2\text{O(aq)} \]  

For the equilibrated saturated solution, one can write

\[ \mu^*_A - \mu^*_{AB} + RT \ln \left( \frac{27m^4\gamma_{\pm}^4}{\gamma_{\mp}} \right) + n\mu^*_A + RT \ln a_A \]  

where \( \mu^*_A, \mu^*_{AB}, \) and \( \mu^*_{AB} \) are, respectively, the standard chemical potentials of the pure solid hydrate (AB), the salt (B) in the infinite dilution reference state, and pure water (A). The solubility of the salt is \( m \) (mol-kg\(^{-1}\)), the mean molal activity coefficient is \( \gamma_{\pm} \), and the activity of water is \( a_A \). The standard Gibbs energy of solution for the lanthanide nitrate hydrate follows from Eq. (3)

\[ \Delta G^o_{\text{soln}} = \mu^*_{B} - \mu^*_{AB} + n\mu^*_A \]  

In terms of ionic and lattice contributions, Eq. (4) can be written as